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The Scattering of Electrons by Hydrocarbon Films

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Several formulae are derived expressing the intensity of electron scattering for a variety of orientations of hydrocarbon films on a solid surface. Intensity contour maps may be constructed from these formulae for arbitrarily chosen models. These maps are helpful for determining the structure of a film and are being prepared for future publication.

CONSIDERABLE attention has been given to the study of the unusual properties of long chain hydrocarbon films on various solid surfaces. An example is the field of boundary lubrication where proper significance has been given to the importance of the strong adhesive forces between an oil film and the metal surface being lubricated.[1] These films are at times perhaps only one molecule thick, oriented so that their long molecular axes are vertical or almost so. Electrons are ideal for studying such films because of their low penetrating power. As a result the major portion of the scattering arises from the outermost layers of atoms when the beam strikes at a glancing angle. Murison,[2] using fast electrons, performed the first experiments on long chain organic compounds. A study of lubricating oils was subsequently made using electron diffraction by Andrew[3] who obtained a correlation between the lubricating qualities of the oils and their corresponding patterns. Another interesting study of surface films has been made by Germer and Storks.[4] They investigated the structure of monomolecular and multimolecular films of barium stearate and stearic acid prepared by the Langmuir-Blodgett technique.

Thus far an expression for the intensity of scattering has been given only for the case where the molecules are distributed randomly about their axes and these axes are normal to the surface of attachment.[2,4] The expressions to be derived below give the intensity of scattering for more general spatial arrangements and by means of these, more detailed information concerning the structure of surface films may be obtained.

MATHEMATICAL DEVELOPMENT

We wish to obtain the intensity of coherent scattering of fast electrons (*ca.* 30,000 volt electrons) by long hydrocarbon chains in arbitrary orientations relative to the surface of attachment. It is assumed that a chain is composed of two parallel rows of carbon atoms in a staggered configuration, and that the contribution from hydrogen atoms and end groups, such as

* This work was performed in the Chemistry Department of the University of Michigan as part of a cooperative project between the University and the Naval Research Laboratory under Contract Number N173s—10452.

[1] For a general discussion containing many references one is referred to the book by N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, New York, 1941). See also *The Chemical Background for Engine Research* (Interscience Publishers, Inc., New York, 1943), "Lubrication," by O. Beeck, page 265.

[2] C. A. Murison, Phil. Mag. **17**, 201 (1934).

[3] L. T. Andrew, Trans. Faraday Soc. **32**, 607 (1936).

[4] L. H. Germer and K. H. Storks, J. Chem. Phys. **6**, 280 (1938).

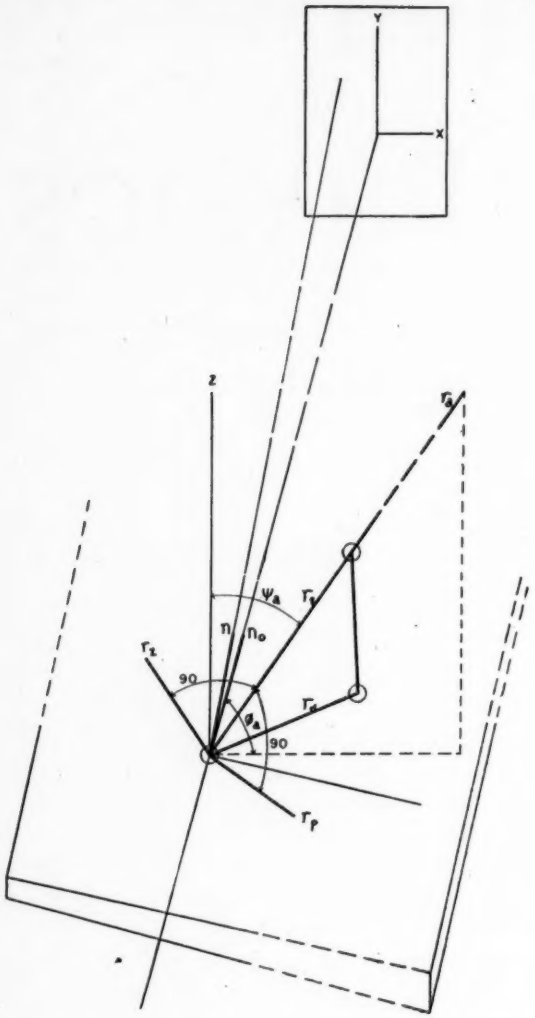

FIG. 1. End of hydrocarbon chain rests on flat surface. The direct beam ($\mathbf{n}_0$) and the scattered beam ($\mathbf{n}$) reach the photographic plate (x, y).

carboxyl, may be neglected. The distribution of the chains is considered to be sufficiently dilute so that each one scatters independently.

In order to discuss the various spatial arrangements which will be considered, we define a set of parameters in terms of which the orientation of the carbon chain may be completely determined. We place the carbon atom closest to the supporting surface at the origin and define the row in which it occurs as the axis of the molecule, vector $\mathbf{r}_a$ (see Fig. 1). The other row of atoms may be free to rotate about this axis and the angle of rotation, δ, is measured relative to a vertical plane containing axis $\mathbf{r}_a$. By fixing the position of $\mathbf{r}_a$ in space and the value of angle δ, the orientation of the carbon chain is determined.

Expressions for the intensity of scattering will be obtained for the following cases:

I. The molecules are fixed in space. Thus, angles ψ_a and ϕ_a, the angles which determine the position of $\mathbf{r}_a$, and angle δ which determines the orientation of the plane of the carbon chain assume specific arbitrary values.[5]

II. The axes of the molecules are arbitrarily fixed in space but the planes of the carbon chains are considered to have random orientations about these axes.[6]

III. The tilt of the molecular axis and the orientation of the plane of the chain are arbitrarily chosen. However, the molecules are randomly oriented about axis z.

IV. The tilt of the molecular axis is arbitrarily fixed. However, the molecules are randomly oriented about the vertical, z, and also about their own axes.

Our next step is to obtain an expression for the amplitude of electron scattering for a generalized molecule consisting of i atoms, bearing in mind that the intensity is equal to the square of the absolute magnitude of the amplitude. The general expression is then applied to the above listed cases for the staggered carbon chain.

We describe by $\mathbf{r}_i$ the vector from the origin to the atom i (see Fig. 2). As an electron beam

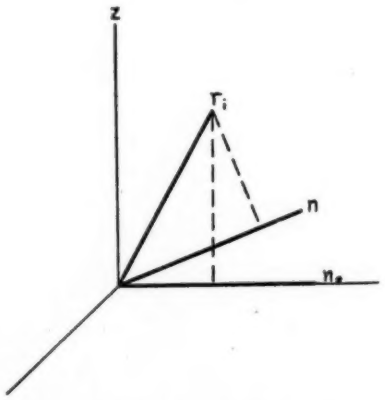

FIG. 2. Vectors defining path difference, $\mathbf{n}\cdot\mathbf{r}_i - \mathbf{n}_0\cdot\mathbf{r}_i$.

[5] Angle ψ_a is the tilt of $\mathbf{r}_a$ from the vertical axis, z, and angle ϕ_a is the clockwise rotation (when looking down on the surface) of the $\mathbf{r}_a z$ plane from the plane bounded by z and the incident beam after traversing the origin, $\mathbf{n}_0 z$.

[6] The case of free rotation about an axis cannot be distinguished from fixed random orientations among the many molecules.

strikes the molecule, each atom scatters a wavelet; and the path difference between the wavelets scattered by the atom at the origin and the atom i is $(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_i$, where $\mathbf{n}$ and $\mathbf{n}_0$ are unit vectors in the direction of the scattered wave and the incident wave, respectively. If the phase of the wavelet scattered at the origin is considered to be zero, the amplitude of the wave scattered by the carbon chain in the direction $\mathbf{n}$ is proportional to

$$\frac{f_c}{r}\sum_{i=1}^{N}\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_i\right], \qquad (1)$$

where f_c is the scattering factor for carbon, a function of $\mathbf{n}$ and $\mathbf{n}_0$, r is the radial coordinate of the scattered beam measured from the origin to any reference point in space (in our case points on the photographic plate), $k=2\pi/\lambda$ where λ is the electron wave-length and N is the number of carbon atoms. The regularity of the structure of the hydrocarbon chain allows one to sum expression (1) as a power series before squaring its absolute value to obtain the intensity of scattering. Cases I and II are then obtained in a compact form. However, for Cases III and IV there is no gain in summing the series and so instead, a general expression for the intensity is obtained from (1) by multiplying it by its complex conjugate. The result is

$$\frac{f_c^2}{r^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_{ij}\right], \qquad (2)$$

where $\mathbf{r}_{ij}$ is a vector connecting the ith and jth atoms. Expression (2) is used for deriving formulae III and IV, resulting in less compact expressions than those of the first two cases.

Case I

The plan of this section is (*a*) to write expression (1) in the form of a power series and sum it, (*b*) to obtain the path differences included in (*a*) in terms of the internal structural parameters of the chain γ_d, r_d, and r_t (defined below), functions of the polar coordinates of the scattered beam, and the orientation parameters ψ_a, ϕ_a, and δ, and (*c*) to insert the results of (*b*) into (*a*) and arrive at an expression for the intensity. Finally the relations between the polar coordinates of the scattered beam and the functions thereof are

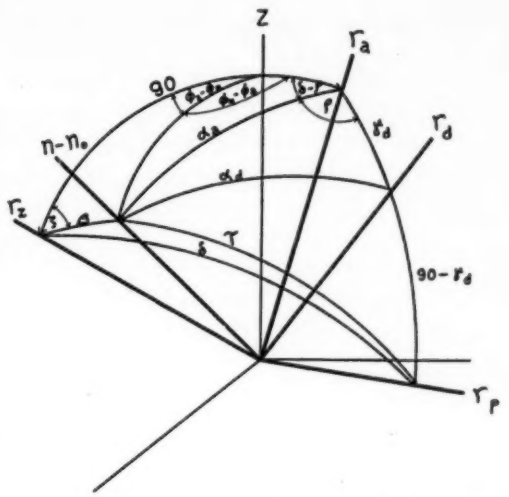

FIG. 3. Trigonometric details at point of scattering.

given. We thus may express the intensity in terms of the internal structural parameters, the orientation parameters, and the coordinates of the scattered beam.

(*a*) We may write expression (1), for a chain containing an even number of carbon atoms, N, in the form of a power series as follows:

$$\frac{f_c}{r}\sum_{g=0}^{N/2-1}\exp\left[ikg(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_t\right]\times\left(1+\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_d\right]\right), \qquad (3)$$

where $\mathbf{r}_d$ is the vector which connects the carbon atom at the origin to the nearest one and $\mathbf{r}_t$ is the vector which connects the carbon atom at the origin to the nearest one in the same row. The sum of (3) is

$$\frac{1-\exp\left[iNk(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_t/2\right]}{1-\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_t\right]}\times\left(1+\exp\left[ik(\mathbf{n}-\mathbf{n}_0)\cdot\mathbf{r}_d\right]\right). \qquad (4)$$

(*b*) The angle between $\mathbf{n}-\mathbf{n}_0$ and $\mathbf{r}_t$ is α_a and the angle between $\mathbf{n}-\mathbf{n}_0$ and $\mathbf{r}_d$ is α_d (see Fig. 3). We proceed to relate these angles to the structural and orientation parameters and functions of the coordinates of the scattered beam. Let us define the following quantities:

$\mathbf{r}_p$ = a vector perpendicular to $\mathbf{r}_a$ in the plane of the carbon chain and placed at the origin.

$\mathbf{r}_z$ = a vector perpendicular to $\mathbf{r}_a$ in the $\mathbf{r}_a z$ plane and placed at the origin.

The angle of rotation of the chain, δ, is clearly the angle between $\mathbf{r}_z$ and $\mathbf{r}_p$.

β = angle between $\mathbf{n}-\mathbf{n}_0$ and $\mathbf{r}_z$.
τ = angle between $\mathbf{n}-\mathbf{n}_0$ and $\mathbf{r}_p$.
γ_d = angle between $\mathbf{r}_a$ and $\mathbf{r}_d$.
ρ = angle between planes defined by $\mathbf{r}_a$ and $\mathbf{r}_d$ and $\mathbf{r}_a$ and $\mathbf{n}-\mathbf{n}_0$.
ζ = angle between planes defined by $\mathbf{r}_a$ and $\mathbf{r}_z$ and $\mathbf{r}_z$ and $\mathbf{n}-\mathbf{n}_0$.
ψ_n = angle of tilt of $\mathbf{n}-\mathbf{n}_0$ from the vertical axis, z.
ϕ_n = angle of rotation of $\mathbf{n}-\mathbf{n}_0$ from the $\mathbf{n}_0 z$ plane.[7]
ψ_z = angle of tilt of $\mathbf{r}_z$ from the vertical axis, z.
ϕ_z = angle of rotation of $\mathbf{r}_z$ from the $\mathbf{n}_0 z$ plane.[7]

From the sine and cosine laws of spherical trigonometry, the following relations are obtained:

$$\begin{aligned}
&\cos\alpha_d=\cos\alpha_a\cos\gamma_d+\sin\alpha_a\sin\gamma_d\cos\rho,\\
&\cos\tau=\sin\alpha_a\cos\rho,\\
&\cos\tau=\cos\delta\cos\beta+\sin\delta\sin\beta\sin\zeta,\\
&\sin\zeta=\sin\alpha_a\sin(\delta-\rho)/\sin\beta,\\
&\cos\alpha_a=\cos\psi_n\cos\psi_a\\
&\qquad\qquad+\sin\psi_n\sin\psi_a\cos(\phi_a-\phi_n),
\end{aligned}\tag{5}$$

and

$$\cos\beta=\cos\psi_n\cos\psi_z+\sin\psi_n\sin\psi_z\cos(\phi_z-\phi_n),$$

where

$$\phi_z=\pi+\phi_a \quad\text{and}\quad \psi_z=90-\psi_a.$$

By combining the first four expressions in (5) we get[8]

$$\cos\alpha_d=k_0+k_1\cos\delta\pm k_2\sin\delta,\tag{6}$$

where

$$k_0=\cos\alpha_a\cos\gamma_d,\quad k_1=\sin\gamma_d\cos\beta,$$

and

$$k_2=\sin\gamma_d\sin\psi_n\sin(\phi_a-\phi_n).$$

(*c*) We multiply (4) by its complex conjugate, introduce the expressions for $\cos\alpha_a$ and $\cos\alpha_d$ obtained in (5) and (6), and find the intensity proportional to[9]

$$2\frac{f_c^2\sin^2(Nsr_t\cos\alpha_a/4)}{r^2\sin^2(sr_t\cos\alpha_a/2)}\times[1+\cos(sr_d\cos\alpha_d)],\tag{7}$$

where $s=k|\mathbf{n}-\mathbf{n}_0|$.

We denote the angular coordinates of the scattered beam, $\mathbf{n}$, by ψ, the tilt from the vertical axis, z, and by ϕ the rotation from the $\mathbf{n}_0 z$ plane using the same conventions as apply to angle ϕ_a. The following readily obtained relations enable us to express (7) and the subsequent expressions in II, III, and IV, in terms of these coordinates.

$$\begin{aligned}
s&=4\pi[1-\cos\phi\sin\psi/2]^{\frac{1}{2}}/\lambda,\\
s\cos\psi_n&=2\pi\cos\psi/\lambda,\\
s\sin\psi_n&=2\pi[2(1-\cos\phi\sin\psi)\\
&\qquad-\cos^2\psi]^{\frac{1}{2}}/\lambda,\\
s\sin\psi_n\cos\phi_n&=-2\pi(1-\cos\phi\sin\psi)/\lambda,\\
s\sin\psi_n\sin\phi_n&=\pm2\pi[2(1-\cos(\pm\phi)\sin\psi)\\
&\qquad-\cos^2\psi-(1-\cos(\pm\phi)\sin\psi)^2]^{\frac{1}{2}}/\lambda.
\end{aligned}\tag{8}$$

[10]

The scattering factor, f_c, may also be expressed in terms of the angular coordinates of the scattered beam since it is equal to $6-F_c/s^2$ where F_c is the x-ray scattering factor for carbon atoms.[11]

Cartesian coordinates may be defined for the photographic plate in terms of the main beam as the origin, an x axis parallel to the plane of the supporting surface and a y axis parallel to the surface normal, z. Since

$$\sin\phi=x/(L^2+x^2)^{\frac{1}{2}}\tag{9}$$

and

$$\cos\psi=y/(L^2+x^2+y^2)^{\frac{1}{2}},$$

where L is the distance from the point of scattering to the origin of the photographic plate, the relations in (8) may be expressed as accurately as desired in terms of x and y. The fact that L is much larger than x or y allows one to make

[7] These angles are measured by the same convention as applies to angle ϕ_a.

[8] The ambiguity regarding the sign may be resolved by defining δ as increasing when the rotation of $\mathbf{\Gamma}_d$ about the axis of the chain, $\mathbf{r}_a$, appears counterclockwise to one observing the tip of $\mathbf{r}_a$ and facing the origin. Then a numerical check shows that the negative sign must be taken.

[9] Note that N is even. When N is odd an expression much less compact than (7) is obtained. Because of the rarity of occurrence of odd chains, it does not seem worth while to discuss this case further at present.

[10] We are interested in the scattered intensities occurring in the solid angle above the undeviated beam included by a photographic plate. Thus, only small values of ϕ are involved. If we mean by $+\phi$ a small clockwise rotation from the $\mathbf{n}_0 z$ plane and $-\phi$ a small counterclockwise rotation, the method for choosing the correct sign of the square root is clear.

[11] See *Internationale Tabellen Zur Bestimmung von Kristallsstrukturen* (J. W. Edwards, Ann Arbor, Michigan, 1944), revised edition, Vol. II, p. 571.

greatly simplifying approximations. Also in practice the change in r may be neglected over the area of a photographic plate ordinarily considered.

Case II

For Case II, an average of the contributions from all positions of the molecule about axis $\mathbf{r}_a$ is required. This is accomplished by integrating (7) with respect to δ, from 0 to 2π, the probability of the chain occurring in any interval δ and $\delta+d\delta$ is $d\delta/2\pi$. We note in (6) that $\cos\alpha_d$ is a function of δ and rewrite it as

$$\cos\alpha_d = k_0 + A\cos(\delta+B), \tag{10}$$

where

$$A=\pm(k_1^2+k_2^2)^{\frac{1}{2}} \quad \text{and} \quad B=\tan^{-1}\frac{k_2}{k_1}.$$

Expression (10) replaces the expression for $\cos\alpha_d$ in (7) and we find that the contribution from all positions about axis $\mathbf{r}_a$ may be obtained from considering the real part of the integral,

$$\exp[isr_dk_0] \times\int_0^{2\pi}\exp[isr_dA\cos(\delta+B)]d\delta/2\pi \tag{11}$$

which has the value,

$$\cos(sr_dk_0)J_0(sr_dA), \tag{12}$$

where J_0 represents the Bessel function of zero order. We thus have from (7) and (12) the desired formula II,

$$2\frac{f_c^2\sin^2(Nsr_t\cos\alpha_a/4)}{r^2\sin^2(sr_t\cos\alpha_a/2)} \times[1+\cos(sr_d\cos\gamma_d\cos\alpha_a) \times J_0(sr_d\sin\gamma_d\sin\alpha_a)], \tag{13}$$

where $\cos\alpha_a$ is defined in (5) and N is even. The relations required for writing (13) in terms of the angular coordinates of the scattered beam, ψ and ϕ are found in (8). The term $s\sin\alpha_a$ can be expressed in terms of ψ and ϕ using s and $s\cos\alpha_a$. Since $J_0(x)=J_0(-x)$, no difficulty results from the ambiguity of sign arising from deriving the sine of an angle from its cosine.

Case III

In order to obtain formulae III and IV we work with expression (2). The vector $\mathbf{r}_d$ in the above analysis can be replaced by the general interatomic vector $\mathbf{r}_{ij}$ and then α_d is replaced by α_{ij} and γ_d by γ_{ij}. We may write instead of expression (6),

$$\cos\alpha_{ij}=H_0+H_1\cos\delta-H_2\sin\delta, \tag{14}$$

where

$$H_0=\cos\alpha_a\cos\gamma_{ij}, \quad H_1=\sin\gamma_{ij}\cos\beta,$$

and

$$H_2=\sin\gamma_{ij}\sin\psi_n\sin(\phi_a-\phi_n).$$

We substitute (14) into (2) and find the intensity proportional to[12]

$$\frac{f_c^2}{r^2}\sum_{i=1}^{N}\sum_{j=1}^{N} \times\exp[isr_{ij}(H_0+H_1\cos\delta-H_2\sin\delta)]. \tag{15}$$

To obtain formula III an average is taken of the contribution from all values of ϕ_a from 0 to 2π. The expressions for $\cos\alpha_a$ and $\cos\beta$ given in (5) are substituted into (15) and we find that we must consider the integral

$$\int_0^{2\pi}\exp[isr_{ij}C\cos(\phi'+D)]d\phi'/2\pi, \tag{16}$$

where

$$\phi'=\phi_a-\phi_n,$$
$$C=\pm([\cos\gamma_{ij}\sin\psi_n\sin\psi_a - \sin\gamma_{ij}\sin\psi_n\cos\psi_a\cos\delta]^2 + [\sin\gamma_{ij}\sin\psi_n\sin\delta]^2)^{\frac{1}{2}}$$

and D is an arc tangent function which disappears, as previously, in the integration. The value of (16) is

$$J_0(sr_{ij}C). \tag{17}$$

Next let us break up the summation over the interatomic distances into two groups, one over the distances along the two rows of atoms and the other over the distances across the rows. If we consider N even, it can be shown that there are

[12] Note that since $\mathbf{r}_{ij}=-\mathbf{r}_{ji}$, expression (2) is real and thus so is (15). It will be convenient henceforth, however, to consider only the contribution from $\mathbf{r}_{ij}$ (when $i\neq j$) and obtain our final result by multiplying the real part of this contribution by 2.

2ν distances of length $(N/2-\nu)r_t$ along the two rows where ν goes from 1 to $(N-2)/2$. Across the rows there are μ distances projected by the cosines of their respective angles γ_{ij}, and have the projected length $([N+1]/2-\mu)r_t$ where μ goes from 1 to $N/2$ and also λ distances of projected length $-([N-1]/2-\lambda)r_t$ as λ goes from 1 to $(N-2)/2$. All the distances across the rows, multiplied by $\sin\gamma_{ij}$, give the inter-row distance.[13] We get for Case III

$$Nf_c^2/r^2+2\frac{f_c^2}{r^2}\sum_{\nu=1}^{(N-2)/2}2\nu\cos[(N/2-\nu)r_t\cos\psi_a s\cos\psi_n]J_0[(N/2-\nu)r_t\sin\psi_a s\sin\psi_n]$$

$$+2\frac{f_c^2}{r^2}\sum_{\mu=1}^{N/2}\mu\cos[([N+1]/2-\mu)r_t\cos\psi_a s\cos\psi_n+r_0\sin\psi_a s\cos\psi_n\cos\delta]$$

$$\times J_0\{s\sin\psi_n([([N+1]/2-\mu)r_t\sin\psi_a-r_0\cos\psi_a\cos\delta]^2+[r_0\sin\delta]^2)^{\frac{1}{2}}\}$$

$$+2\frac{f_c^2}{r^2}\sum_{\lambda=1}^{(N-2)/2}\lambda\cos[-([N-1]/2-\lambda)r_t\cos\psi_a s\cos\psi_n+r_0\sin\psi_a s\cos\psi_n\cos\delta]$$

$$\times J_0\{s\sin\psi_n([-([N-1]/2-\lambda)r_t\sin\psi_a-r_0\cos\psi_a\cos\delta]^2+[r_0\sin\delta]^2)^{\frac{1}{2}}\}, \quad (18)$$

where r_0 is the inter-row distance. The factor 2 appears since all interatomic distances are counted twice in the double summation. By using (8), expression (18) may be given in terms of the angular coordinates of the scattered beam, ϕ and ψ.

Case IV

It would seem natural to obtain formula IV from formula III directly by integrating with respect to δ to get the average contribution from random positions about $\mathbf{r}_a$. However, a formula which appears more simple to calculate is obtained if one reverses the order of integrating, that is to derive the average contribution from random positions about $\mathbf{r}_a$ first and then the average contribution from random positions about z. We note that (14) may be written

$$\cos\alpha_{ij}=H_0+E\cos(\delta+F), \quad (19)$$

where

$$E=\pm(H_1^2+H_2^2)^{\frac{1}{2}} \quad \text{and} \quad F=\tan^{-1}(H_2/H_1).$$

We have by substituting this into (2)

$$\frac{f_c^2}{r^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp[isr_{ij}(H_0+E\cos[\delta+F])]. \quad (20)$$

The average over all values of δ is obtained from considering the integral,

$$\int_0^{2\pi}\exp[isr_{ij}E\cos(\delta+F)]d\delta/2\pi, \quad (21)$$

whose value is $J_0(sr_{ij}E)$. The contribution from the rotation of the chain about axis $\mathbf{r}_a$ is then

$$\frac{f_c^2}{r^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp[isr_{ij}\cos\gamma_{ij}\cos\alpha_a]J_0(sr_{ij}\sin\gamma_{ij}\sin\alpha_a). \quad (22)$$

[13] The case when N is odd is readily considered. There are $2\nu-1$ distances of length $([N+1]/2-\nu)r_t$ along the two rows where ν goes from 1 to $(N-1)/2$. Across the rows there are μ distances projected by the cosines of their respective angles, γ_{ij}, and have the projected length $(N/2-\mu)r_t$ as μ goes from 1 to $(N-1)/2$ and also λ distances of projected length $-(N/2-\lambda)r_t$ as λ goes from 1 to $(N-1)/2$.

Let us now split the above summation among distances along the two rows of atoms and those across the rows (neglecting for the present terms for which $i=j$, the atomic scattering). We get

$$2\frac{f_c^2}{r^2}\sum_{\nu=1}^{(N-2)/2} 2\nu \exp\left[i(N/2-\nu)r_t s\cos\alpha_a\right]+2\frac{f_c^2}{r^2}\sum_{\mu=1}^{N/2}\mu\exp\left[i([N+1]/2-\mu)r_t s\cos\alpha_a\right]J_0(sr_0\sin\alpha_a)$$

$$+2\frac{f_c^2}{r^2}\sum_{\lambda=1}^{(N-2)/2}\lambda\exp\left[-i([N-1]/2-\lambda)r_t s\cos\alpha_a\right]J_0(sr_0\sin\alpha_a). \quad (23)$$

We now wish to obtain the average contribution from all possible values of ϕ_a. The expression for $\cos\alpha_a$ is substituted into the first summation in (23) and it is found that we must consider the integral,

$$\int_0^{2\pi}\exp\left[i(N/2-\nu)r_t s\sin\psi_n \times\sin\psi_a\cos(\phi_a-\phi_n)\right]d\phi_a/2\pi. \quad (24)$$

Its value is

$$J_0([N/2-\nu]r_t\sin\psi_a s\sin\psi_n). \quad (25)$$

For the second and third summations in (23) we must obtain a useful expansion for $J_0(sr_0\sin\alpha_a)$. We have

$$\begin{aligned}\sin\alpha_a&=(1-\cos^2\alpha_a)^{\frac{1}{2}}\\&=(P-Q\cos(\phi_a-\phi_n)\\&\qquad -R\cos^2(\phi_a-\phi_n))^{\frac{1}{2}},\end{aligned} \quad (26)$$

where

$$\begin{aligned}P&=1-\cos^2\psi_n\cos^2\psi_a,\\Q&=2\cos\psi_n\cos\psi_a\sin\psi_n\sin\psi_a,\\R&=\sin^2\psi_n\sin^2\psi_a.\end{aligned}$$

The above expression may be approximated by neglecting R. This imposes a strict limitation on the applicability of the final formula. An estimate may be made of this limitation by setting $\phi_a-\phi_n$ equal to 0° or 180° and calculating the values of $P, Q,$ and R for some typical cases. It is found that if one assumes a value of 20° for angle ψ_a, the area enclosed in $-1.5<x<1.5$ cm and $1<y<4$ cm may be covered with an error in the intensity probably not greater than 10 percent in the vicinity of the main maxima, and usually much less. In the region mentioned the approximation improves with larger y and smaller x since $\sin\psi_n$ is very nearly $x/(x^2+y^2)^{\frac{1}{2}}$.

We may write

$$\sin\alpha_a=[a^2+b^2-2ab\cos(\phi_a-\phi_n)]^{\frac{1}{2}}, \quad (27)$$

where

$$a^2=[P+(P^2-Q^2)^{\frac{1}{2}}]/2$$

and

$$b^2=Q^2/[2P+2[P^2-Q^2]^{\frac{1}{2}}].$$

From the addition theorem for J_0, we get

$$J_0(sr_0\sin\alpha_a)=\sum_{m=0}^{\infty}\epsilon_m J_m(sr_0a)J_m(sr_0b)\cos m(\phi_a-\phi_n), \quad (28)$$

where ϵ_m is equal to unity when $m=0$ and is equal to 2 for all other values of m.[14] By substituting (28) into the second summation of (23) the following integral arises from considering the contribution from all values of ϕ_a,

$$\int_0^{2\pi}\exp\left[i([N+1]/2-\mu)r_t\sin\psi_a s\sin\psi_n \times\cos(\phi_a-\phi_n)\right]\cos m(\phi_a-\phi_n)d\phi_a/2\pi. \quad (29)$$

Its value is

$$(i)^m J_m[([N+1]/2-\mu)r_t\sin\psi_a s\sin\psi_n]. \quad (30)$$

Clearly, a similar integral arises for the third summation whose value is

$$(i)^m J_m[-([N-1]/2-\lambda)r_t\sin\psi_a s\sin\psi_n]. \quad (31)$$

From the results, (25), (30), and (31) and the terms in (23) which were constant with respect to the integration over ϕ_a, we may now write down formula IV. (The contributions from the second and third summations in (23) may be combined since $J_\nu(-z)=-J_\nu(z)$ if ν is odd and $J_\nu(-z)=J_\nu(z)$ if ν is even.[13])

[14] My thanks to Professor Otto Laporte for suggesting this expansion.

$$N\frac{f_c^2}{r^2}+2\frac{f_c^2}{r^2}\sum_{\nu=1}^{(N-2)/2} 2\nu\cos[(N/2-\nu)r_t\cos\psi_a s\cos\psi_n]J_0[(N/2-\nu)r_t\sin\psi_a s\sin\psi_n]$$
$$+\frac{2f_c^2}{r^2}\sum_{\mu=1}^{N/2}(2\mu-1)\cos[([N+1]/2-\mu)r_t\cos\psi_a s\cos\psi_n]$$
$$\times\sum_{m=0}^{\infty}(-1)^m\epsilon_m J_{2m}(sr_0a)J_{2m}(sr_0b)J_{2m}[([N+1]/2-\mu)r_t\sin\psi_a s\sin\psi_n]$$
$$+\frac{2f_c^2}{r^2}\sum_{\mu=1}^{N/2}(2\mu-1)\sin[([N+1]/2-\mu)r_t\cos\psi_a s\cos\psi_n]$$
$$\times\sum_{m=0}^{\infty}(-1)^{m+1}2J_{2m+1}(sr_0a)J_{2m+1}(sr_0b)J_{2m+1}[([N+1]/2-\mu)r_t\sin\psi_a s\sin\psi_n]. \quad (32)$$

Expression IV, though quite complex, permits calculation of the intensity distribution from a chosen structure. Examination shows that, within the range of validity mentioned above, the arguments sr_0a and sr_0b are sufficiently small to cause the infinite series to converge very rapidly.

Because of the small value of $\sin\psi_n$ for points along the y axis, formulae III and IV will be indistinguishable from formulae I and II, respectively. In other words the intensity along the y axis is virtually independent of the variable ϕ_a.

Additional Remarks

The intensity from a molecule with $\mathbf{r}_a$ vertical has been previously obtained.[2,4] For the case when the plane of the molecule is rotated ϕ_d degrees from the $\mathbf{n}_0z$ plane (measured according to previous conventions) we have

$$\frac{f_c^2\sin^2(Nr_t s\cos\psi_n/4)}{r^2\sin^2(r_t s\cos\psi_n/2)}\times(1+\cos[r_d s\cos\psi_n\cos\gamma_d + r_d s\sin\psi_n\sin\gamma_d\cos(\phi_n-\phi_d)]). \quad (33)$$

By integrating (33) with respect to ϕ_d from 0 to 2π we get

$$\frac{f_c^2\sin^2(Nr_t s\cos\psi_n/4)}{r^2\sin^2(r_t s\cos\psi_n/2)}\times(1+\cos[r_d\cos\gamma_d s\cos\psi_n]\times J_0[r_d\sin\gamma_d s\sin\psi_n]) \quad (34)$$

for the intensity when there is free rotation about $\mathbf{r}_a$. Expression (34) agrees with the result of Germer and Storks when given in terms of the coordinates of the photographic plate, making suitable approximations.

DISCUSSION

For the purpose of interpreting diffraction patterns produced by chains tilted away from the normal, the effect on scattering of only one of the two rows of carbon atoms in a hydrocarbon chain has been used. This has been successful in locating the main maxima. However, subtle effects on the intensity of the interaction of the two rows of the staggered chain could not be anticipated. The formulae obtained above which take into account the effect of both rows give the scattered intensity for some of the more interesting spatial orientations. They are, of course, not exhaustive. For instance, expressions were not obtained for the average effect of a variation in angle ψ_a, the tilt from the vertical, through a small angle range.

It was previously noted that fixed random positions of the molecules about an axis is mathematically indistinguishable from the case of free rotation of each molecule about this axis. Thus the same pattern can be expected from both cases. Another situation which appears at first glance indistinguishable from the previous two is the case in which there are small patches on a surface in which all the molecules have the same orientation, but the orientation varies from patch to patch. This case, however, would probably arise when the density of packing approaches that present in a crystal. Thus, such an arrangement of the molecules could affect the intensity of scattering because of their repeated intermolecular distances. This effect is not included in the above formulae. Instead, the latter are

derived on the assumption that the distribution of molecules is sufficiently dilute to make intermolecular interaction negligible. A lack of agreement, therefore, between the scattered intensity calculated from the theoretical formulae and that actually found may be caused by a close packing of the molecules. This effect has already been suggested.[4]

When making calculations for contour maps of the intensity, it is very helpful to know the region in which the main maxima occur. The formulae for the intensity, conveniently expressed in terms of the plate coordinates, x and y, may then be considered in fairly restricted areas.[15] Such calculations are being made at present in this laboratory for future publication.

[15] The following useful tables are available: (*a*) Tables of Sines and Cosines for Radian Arguments, Federal Works Agency Work Projects Administration, Project No. 765-97-3-10, New York, 1940. (*b*) Hague, Proc. Phys. Soc. **29**, 211 (1917). (*c*) Gray, Mathews, and MacRobert, *A Treatise on Bessel Functions* (The Macmillan Company, New York, 1931), p. 286.

An improvement in interpretation can be expected from a method of photographing which would allow for quantitative measurements of the intensity. P. P. Debye[16] has suggested the use of a rotating sector in gas diffraction to eliminate the effect of the scattering factors. In our case only one occurs, f_c. It would appear that hydrocarbon films are unusually suited for use by the sector method since one sector would suffice for all films, the radiation allowed to pass through being inversely proportional to $(6-F_c)^2/s^4$. In addition the difficulty of vapors diffusing into the camera on long exposure, as occurs in gas diffraction, does not arise.

For his interest I wish to thank Professor Lawrence O. Brockway who has directed the work performed in the Chemistry Department of the University of Michigan under contract with the Naval Research Laboratory.

[16] P. P. Debye, Physik. Zeits. **40**, 66 and 404 (1939).

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A Relation between Bond Force Constants, Bond Orders, Bond Lengths, and the Electronegativities of the Bonded Atoms

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A relation of the form

$$k = aN(x_A x_B/d^2)^{\frac{3}{4}} + b$$

has been found to hold accurately for a large number of diatomic and simple polyatomic molecules in their ground states. (The average deviation of k calculated from k observed for seventy-one cases is 1.84 percent.) Here k is the bond-stretching force constant, d the bond length, N the bond order, and x_A and x_B are the electronegativities of the bonded atoms. If k is measured in dynes/cm$\times 10^{-5}$ and d in Angstrom units, a and b have the values 1.67 and 0.30, respectively, for stable molecules exhibiting their normal covalencies, except those in which both bonded atoms have only one electron in the valence shell; for diatomic molecules of the alkali metals, Na_2, NaK, etc., a and b are 1.180 and -0.013, respectively; for hydrides of elements having a single electron in the valence shell, 1.180 and 0.040, respectively; and for diatomic hydrides of elements having two to four electrons in the valence shell, 1.42 and 0.08, respectively. Numerous applications of the relation are made and certain exceptions are pointed out.

DESCRIPTION OF THE RELATION

SEVERAL relations[1,2] between force constants or vibrational frequencies and bond distances have been found to hold approximately for a limited number of molecules. They, in general,

[1] P. M. Morse, Phys. Rev. **34**, 57 (1929); D. Clark, Phil. Mag. **18**, 459 (1934); H. S. Allen and A. K. Longair, Phil. Mag. **19**, 1032 (1935); M. L. Huggins, J. Chem. Phys. **3**, 473 (1933); **4**, 308 (1936); J. J. Fox and A. E. Martin, J. Chem. Soc. 884 (1939); G. B. B. M. Sutherland, J. Chem. Phys. **8**, 161 (1940); J. W. Linnett, Trans. Faraday Soc. **36**, 1123 (1940); C. K. Wu and Chang-Tsing Yang, J. Phys. Chem. **48**, 295 (1944).

[2] R. M. Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).

have two or more parameters that depend on the atoms forming the bond, or their position in the periodic table. The most widely used of these seems to be that of Badger,[2]

$$k_e=(c_{ij}/r_e)^{\frac{1}{3}}+d_{ij},$$

where c_{ij} and d_{ij} are the parameters and r_e and k_e the equilibrium bond distance and bond-stretching force constants, respectively.

Remick[3] has correctly ascribed the increasing force constants of the series CH<NH<OH<FH partly to the increasing electronegativities of the series C<N<O<F, on the basis that the displacement of H would in turn cause a displacement of the valence electrons in the potential field of the heavier atom. In a vibratory link A−B both A and B are displaced with respect to the center of gravity of the bonding electron cloud, and it seems that the bond-stretching force constant k would vary with the electronegativities of both A and B and could be expressed as some function of their product,

$$k=f(x_Ax_B).$$

It is well known that k increases with bond order, that, other things being equal, a double bond is stronger than a single bond, a triple bond stronger than a double bond; and the bond order, which I shall designate as N, may be regarded as a relative measure of the electronic cloud effective in holding the two atoms together.

Thus k varies with all the quantities—N, x_Ax_B, and d—and it should be possible therefore to express it as a combined function,

$$k=f(N, x_Ax_B, d).$$

Though the assumption of such a relationship may be justified by qualitative considerations, a theoretical derivation of the function may not be possible. In the present study the function is evaluated empirically by the correlation of the quantities involved for a large number of molecules in their ground states. It is not possible to check it for the different excited states of one and the same molecule because values for N and x are available for ground states only. The form of the function is:

$$k=aN(x_Ax_B/d^2)^{\frac{1}{3}}+b, \qquad (I)$$

where a and b are constants for certain broad classes of molecules; N, k, and d are the bond order, bond-stretching force constant, and bond distance, respectively; and x_A and x_B are the electronegativities of the atoms A and B.

The constants a and b in the above equation have the same values for stable bonds of atoms exhibiting their normal covalencies, except those in which both atoms have a single electron in the valence shell. Most of the simple molecules with bonds of this type, for which k, N, and d are known with reasonable accuracy, are listed in Table I. Their experimentally observed bond-stretching force constants are compared with those computed from the equation,

$$k=1.67N(x_Ax_B/d^2)^{\frac{1}{3}}+0.30. \qquad (IA)$$

Here k is measured in dynes/cm$\times10^{-5}$ and d in Angstrom units. Specific values of N, k, and d which were used for the calculations are listed in Tables I and VI. The electronegativity values are those found in column 3 of Table VIII.

An examination of the types of molecules in Table I will be helpful in judging for what other molecules Eq. (IA) may be expected to apply. It may not be applied to polyatomic molecules in which there are appreciable interactions between non-bonded atoms, as it assumes a characteristic bond-stretching constant which depends wholly on the properties of the two atoms forming the bond. Polyatomic molecules for which the valence force field function is inadequate may not, in general, be expected to fit the rule. Odd molecules or molecular links of atoms with unsatisfied valencies also seem to be exceptions. Certain classes of these may, nevertheless, be made to fit approximately the more general relation (I) with a proper choice of values for a and b.

For diatomic molecules of the alkali metals, Na_2, NaK, etc., relation (I) has the form,

$$k=1.180(x_Ax_B/d^2)^{\frac{1}{3}}-0.013. \qquad (IB)$$

Table II will illustrate how accurately it holds.

Diatomic hydrides having one electron in the valence shell fit accurately relation (I) in the form,

$$k=1.180(x_Ax_B/d^2)^{\frac{1}{3}}+0.040. \qquad (IC)$$

See Table III.

[3] A. E. Remick, *Electronic Interpretations of Organic Chemistry* (John Wiley & Sons, Inc., New York, 1943), p. 170.

TABLE I. Observed and calculated bond-stretching force constants.

Molecule	Link	Bond order N	Bond-stretching force constant in dynes/cm $\times 10^{-5}$ k obs.	k calc.[a] by Eq. (IA)	Gordy k calc. from k obs. % dev.	k calc. by Badger's rule	Badger k calc. from k obs. % dev.
AsH_3	AsH	1.00	2.81[e]	2.84	1.1	2.47	12.1
B_2H_6	BH	1.00	3.9[f]	4.0	2.6	3.1	20.5
BeO	BeO	2.00	7.50[g]	7.57	.9	6.75	10.0
Br_2	BrBr	1.00	2.46[g]	2.50	1.6	2.48	.8
CH_3Br	CBr	1.00	3.13[h]	3.03	3.2	2.04	34.8
C_2H_2	CC	3.00[b]	15.7[i]	15.7	.0	13.0	17.2
C_2H_4	CC	2.12[b]	9.79[i]	9.70	.9	6.78	30.8
C_2H_6	CC	1.11[b]	4.50[j]	4.21	6.4	2.87	36.2
CH_3CCH	CC	2.89[b]	15.6[k]	15.1	3.2	12.5	19.8
CH_3CCH	C*C	1.23[b]	5.18[k]	5.28	1.9	3.92	24.3
C_6H_6	CC	1.78[b]	7.58[l]	7.69	1.5	5.20	31.4
CH_3Cl	CCl	1.00	3.64[h]	3.54	2.7	2.68	26.4
CH_3F	CF	1.00	5.96[h]	6.02	1.0	5.07	14.9
CH_4	CH	1.00	5.45[m]	5.51	1.1	4.27	21.6
HCN	C*H	1.00	6.20[n]	6.22	.3	4.94	20.3
C_2H_2	C*H	1.00	6.24[n]	6.22	.3	4.94	20.8
CH_3NH_2	CN	1.00	4.86[o]	4.60	5.3	3.78	22.2
HCN	CN	3.00	18.1[p]	18.8	3.9	17.5	3.3
H_2CO	CO	2.00	13.4[i]	13.1	2.2	12.5	6.7
CH_3OH	CO	1.00	5.00[q]	5.28	5.6	4.44	11.2
C_2H_6S	CS	1.00	3.05[r]	3.05	.0	2.25	26.2
CS_2	CS	2.00	7.47[s]	7.37	1.3	7.09	5.1
C_2H_6Se	CSe	1.00	2.59[r]	2.70	4.2	1.84	29.0
Cl_2	ClCl	1.00	3.29[g]	3.35	1.8	2.92	11.2
GeH_4	GeH	1.00	2.78[t]	2.73	1.8	3.26	17.3
HBr	HBr	1.00	4.11[g]	4.06	1.2	4.24	3.2
HCl	HCl	1.00	5.15[g]	4.94	4.1	5.66	9.9
HF	HF	1.00	9.67[g]	9.70	.3	9.43	2.5
HI	HI	1.00	3.14[g]	3.14	.0	[d]	
IBr	IBr	1.00	2.07[g]	2.10	1.9	[d]	
ICl	ICl	1.00	2.39[g]	2.39	.0	2.17	9.2
I_2	II	1.00	1.72[g]	1.77	2.9	1.58	8.1
KBr	KBr	1.00	(.83)[g]	.90	(8.4)[e]	.42	(49.4)[e]
KCl	KCl	1.00	(.85)[g]	.99	(16.5)[e]	[d]	
KI	KI	1.00	.79[g]	.78	1.3	[d]	
NaBr	NaBr	1.00	1.04[g]	1.07	2.9	[d]	
NaCl	NaCl	1.00	1.18[g]	1.18	.0	.59	50.0
NaI	NaI	1.00	.94[g]	.91	3.2	.45	52.1
N_2	NN	3.00	22.9[g]	22.7	.9	26.0	13.6
NH_3	NH	1.00	6.86[e]	6.81	.7	5.94	13.3
H_2O	OH	1.00	8.23[u]	8.24	.1	7.69	6.5
OF_2	OF	1.00	7.67[v]	7.38	3.8	4.79	37.6
OCl_2	OCl	1.00	4.82[w]	4.69	2.7	3.78	21.6
PH_3	PH	1.00	3.33[e]	3.24	2.7	2.87	13.8
H_2S	SH	1.00	4.25[x]	4.14	2.6	4.43	4.2
H_2Se	SeH	1.00	3.37[y]	3.30	2.1	2.73	19.0
H_2S_2	SS	1.00	2.52[r]	2.59	2.8	2.30	8.7
SiH_4	SiH	1.00	2.95[z]	2.92	1.0	2.88	2.4
				Average % deviation	2.0	Average % deviation	17.8

* The effects of triple bond character on the electronegativity of C are taken into account. See discussion in section on electronegativity.

[a] Bond distances used in calculations are listed in Table VI, column 3; electronegativities in Table VIII, column 3; bond orders in column 3 of this table.

[b] From R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. **63**, 41 (1941).

[c] Omitted in computing average deviation.

[d] Badger gives no constants for this combination of period and row of the atomic table.

[e] J. Howard, J. Chem. Phys. **3**, 208 (1935). The value given is increased 8 percent to correct for anharmonicity.

[f] See reference 29 in text.

[g] Computed from the ω_e values selected by G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 483.

[h] B. L. Crawford and S. R. Brinkley, Jr., J. Chem. Phys. **9**, 69 (1941).

[i] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **148**, 250 (1935).

[j] F. Stitt, J. Chem. Phys. **7**, 297 (1939).

[k] B. L. Crawford, J. Chem. Phys. **8**, 526 (1940).

[l] R. C. Lord and D. H. Andrews, J. Phys. Chem. **41**, 149 (1938).

[m] Computed from the ω_1 given by D. M. Dennison (Rev. Mod. Phys. **12**, 175 (1940)) using the formula $\omega_1=(1/2\pi)(k/M_H)$.

[n] T. A. You Wu and A. T. Kiang, J. Chem. Phys. **7**, 178 (1938).

[o] J. T. Edsall, J. Chem. Phys. **5**, 225 (1937).

[p] P. F. Bartunek and E. F. Barker, Phys. Rev. **48**, 516 (1935).

[q] See reference 10 in text.

[r] K. W. F. Kohlrausch, *Raman Spectra* (Akademische Verlagsgesellschaft Becker and Erler, Leipzig, 1943), p. 184.

[s] G. Glockler and T. Y. Tung, J. Chem. Phys. **13**, 388 (1945).

[t] J. W. Straley, C. H. Tindal, and H. H. Nielsen, Phys. Rev. **62**, 161 (1942). The value given is increased 8 percent to correct for anharmonicity.

[u] L. G. Bonner, Phys. Rev. **46**, 458 (1934).

[v] Computed from the valence force field formula,

$$\nu_3=(1/2\pi)\,[k(1/M_A)+((1-\cos\alpha)/M_B)]^{\frac{1}{2}},$$

taking ν_3 as 1280 cm^{-1} and the vertex angle α measured by electron diffraction, 100°.

[w] Computed as described in footnote v of Table I, taking ν_3 as 973 cm^{-1} and the vertex angle α measured by electron diffraction, 115°.

[x] C. R. Bailey, J. W. Thompson, and J. B. Hale, Phys. Rev. **49**, 777 (1936).

[y] D. M. Cameron, W. C. Sears, and H. H. Nielsen, J. Chem. Phys. **7**, 994 (1942). The value given is increased 8 percent to correct for anharmonicity.

[z] C. H. Tindal, W. H. Straley, and H. H. Nielsen, Phys. Rev. **62**, 151 (1942). The value given is increased 8 percent to correct for anharmonicity.

TABLE II. Observed and calculated force constants and bond distances of alkali metals.

Molecule	Force constant in dynes/cm $\times 10^{-5}$ k obs.[a]	Bond distance d obs. in A	k cal. by Eq. (IB)	k calc. from k obs. % dev.	d calc. by Eq. (IB)	d calc. from d obs. % dev.
Cs_2	0.069	4.50[b]	0.067	2.9	4.44	1.3
K_2	.099	3.923[c]	.096	3.0	3.845	2.0
Li_2	.254	2.672[c]	.238	(6.3)[e]	2.558	(4.3)[e]
LiCs	.109	3.75[d]	.113	3.7	3.83	2.1
LiK	.148	3.30[d]	.147	.7	3.29	.3
LiRb	.129	3.50[d]	.131	1.6	3.53	.9
Na_2	.172	3.079[c]	.173	.6	3.096	.6
NaCs	.108	3.76[d]	.108	.0	3.75	.3
NaK	.130	3.50[d]	.128	1.5	3.47	.9
NaRb	.120	3.59[d]	.120	.0	3.59	.0
Rb_2	.081	4.22[b]	.081	.0	4.22	.0
RbCs	.075	4.36[d]	.074	1.3	4.31	1.1
			Average % deviation	1.39	Average % deviation	0.86

[a] Computed from the ω_e values of G. Herzberg, reference 5 in text.
[b] Added radii. See V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).
[c] From G. Herzberg, reference 5 in text.
[d] Determined by Schomaker and Stevenson (J. Am. Chem. Soc. **63**, 37 (1941)) from Badger's rule with its parameters fitted to the similar molecules—Li_2, Na_2, and K_2.
[e] Omitted in computing average deviation.

Diatomic hydrides of elements having two to four electrons in the valence shell may be grouped together and fitted approximately to

$$k = 1.42(x_A x_B/d^2)^{\frac{3}{4}} + 0.08. \qquad \text{(ID)}$$

Results are shown in Table IV.

In all the above forms of relation (I), k is in dynes/cm $\times 10^{-5}$, d in Angstroms, and the x values those of column 3, Table VIII. These units are used throughout the paper.

FORCE CONSTANTS

One use of relation (I) is for the determination of force constants and thus for the estimation of fundamental frequencies associated with the stretching of bonds. Frequently it is a difficult or impossible task to decide which of the many frequencies of a polyatomic molecule are the fundamentals associated with the stretching of bonds. From x-ray and electron diffraction measurements the bond distances in a large number of polyatomic molecules are now known with an accuracy of 1 percent to 3 percent. The bond distances of many others can be estimated with a fair degree of certainty from the additivity rule.[4] Electronegativity values of nearly all the common elements are available. Perhaps the chief difficulty in using the relation to estimate k is the uncertainty of the bond order N for many bonds which are of fractional order.

Accuracy of the Relation

Table I gives a comparison of the force constants calculated from Eq. (IA) with those obtained directly from the observed spectra. Tables II to IV show similar comparisons for k's computed from Eqs. (IB)–(ID), respectively. The differences of the two values, k computed and k observed, are for most of the cases listed in Tables I–IV no greater than the probable error in the observed k's, the average deviation for the seventy-one bonds being only 1.84 percent. Only three of the seventy-five computed k's, those for KBr, KCl, and SiH, deviate more than 6.4 percent from the observed values, and it seems probable that the wide deviation in these may be due to errors in the observed k's. For example, the ratios of the observed k's of KI, KBr, and KCl are not of the proper magnitude when compared to those of NaI, NaBr, and NaCl; whereas the computed values have the expected ratios. The ω_e value used to compute SiH is listed as uncertain by Herzberg.[5]

Though Badger's rule[2] is of advantage in the estimation of bond distances, force constants computed from it differ so much from the ob-

TABLE III. Observed and calculated force constants and bond distances of diatomic hydrides of elements with one electron in the valence shell.

Molecule	Force constant in dynes/cm $\times 10^{-5}$ k obs.[a]	Bond distance d obs.[b] in A	k calc. by Eq. (IC)	k calc. from k obs. % dev.	d calc. by Eq. (IC)	d calc. from d obs. % dev.
CsH	0.467	2.494	0.466	0.2	2.488	0.2
RbH	.514	2.368	.514	.0	2.368	.0
H_2	5.759	.741	5.791	.6	.744	.4
KH	.560	2.244	.564	.7	2.254	.4
LiH	1.026	1.596	1.033	.7	1.602	.4
NaH	.779	1.888	.781	.3	1.892	.2
			Average % deviation	0.42	Average % deviation	0.27

[a] Computed from ω_e values of G. Herzberg, reference 5 in text.
[b] From G. Herzberg, reference 5 in text.

[4] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 153; V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).
[5] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 483.

served values as to make it of questionable value in the computation of unknown k's. This fact has been pointed out previously by Penney and Sutherland.[6] Other rules, such as the Clark relation,[1] in which k is expressed as an inverse 5th or 6th power of d cannot be accurate for the computation of k because the errors in d are multiplied several times in the evaluation of k. The advantage of the present relation for the computation of k is that none of the quantities involved in the expression for k are raised to high powers.

Observed Force Constants Used for Comparison

Some discussion of the observed force constants used for testing the relation is justified. Those of all diatomic molecules and of all M−H bonds in polyatomic molecules are for vibrations of infinitesimal amplitudes. Since vibration constants involving the light hydrogen atoms are appreciably affected by anharmonicity, it was necessary to estimate a correction term for these when the values found in the literature were not for vibrations of infinitesimal amplitude. The correction of +8 percent was determined by averaging the anharmonic effects in the M−H bonds of the molecules for which the correct constants are known.

The simplest molecule containing a given bond of known constants was chosen as representative of that bond, and the same link with the same bond order in other molecules was not repeated except for the case of acetylenic CH. Single bonds to acetylenic carbon, ≡C−, were regarded as different from other single bonds to carbon because of the effective difference in the electronegativity of the carbon in the two cases.

The force constants of the diatomic molecules were computed with the simple harmonic formula,

$$\omega_e = (1/2\pi)(k/\mu)^{\frac{1}{2}},$$

from the ω_e values selected by Herzberg.[5] The k's of polyatomic molecules were chosen from the literature referred to in the table and were computed by the various authors on the assumption of a valence force field function, or a slightly modified form of this function. This treatment assumes that the fundamental vibrations of the molecules are controlled entirely by the stretching and bending of the chemical bonds, that the interactions between non-bonded atoms are negligible. Constants for several of the polyatomic molecules have been computed by more than one researcher. In general the agreement of the different values is sufficiently close for the accuracy required here. Those for such complex molecules as CH_3OH, CH_3NH_2, C_2H_6S, C_2H_6Se cannot be regarded as very accurate. Rather wide disagreement exists in the literature for OCl_2 and OF_2, because of the fact that different workers have assigned the fundamentals differently. Sutherland and Penney[7] have criticized the assignments of Hettner, Pohlman, and Schumacher[8] and have suggested an alternative assignment. Relation (IA) agrees with the Sutherland and Penney values for OCl_2 but with the Hettner, Pohlman, and Schumacher assignment for ν_3 of OF_2. There is sufficient interaction between the hydrogens of the two CH_3 groups of ethane that a modified form of the valence force field is required to compute the observed frequencies satisfactorily.[9] This interaction no doubt causes some deviation from

TABLE IV. Observed and calculated force constants and bond distances of diatomic hydrides of elements with two to four electrons in the valence shell.

Molecule	Force constants in dynes/cm ×10⁻⁵ k obs.[a]	Bond distance d obs.[b] in A	k calc. by Eq. (1D)	k calc. from k obs. % dev.	d calc. by Eq. (1D)	d calc. from d obs. % dev.
AlH	1.62	1.646	1.69	4.3	1.693	2.9
BH	3.04	1.233	3.04	.0	1.233	.0
BaH	.81	2.232	.78	3.7	2.184	2.1
BeH	2.26	1.343	2.20	2.7	1.321	1.6
CH	4.37	1.120	4.34	.7	1.115	.4
CaH	.98	2.002	.97	1.0	1.978	1.1
MgH	1.28	1.731	1.34	4.7	1.789	3.3
SiH	(2.48)	1.521	2.15	(13.3)	(1.380)	(9.3)
SrH	.85	2.146	.88	3.5	2.195	2.3
			Average % deviation	2.58	Average % deviation	1.71

[a] Computed from ω_e values of G. Herzberg, reference 5 in text.
[b] From G. Herzberg, reference 5 in text.

[6] W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. **156**, 654 (1936).

[7] G. B. B. M. Sutherland and W. G. Penney, Proc. Roy. Soc. **156**, 678 (1936).

[8] G. Hettner, R. Pohlman, and H. I. Schumacher, Zeits. f. Physik. **96**, 203 (1935).

[9] F. Stitt, J. Chem. Phys. **7**, 297 (1939).

TABLE V. Predicted force constants and vibrational frequencies.

Molecule	Link	Bond length in A d obs.	Bond-stretching force constant calculated[a] from Eq. (IA) in dynes/cm $\times 10^{-5}$	Expected frequency cm^{-1}
CsBr	CsBr	3.14[e]	0.82	168
CsCl	CsCl	3.06[e]	.87	226
CsI	CsI	3.41[e]	.72	137
F_2	FF	1.435[d]	7.93	1190
Ge_2H_6	GeGe	2.41[e]	1.29	238
RbBr	RbBr	2.94[e]	.89	192
RbCl	RbCl	2.89[e]	.94	248
RbI	RbI	3.26[e]	.76	159
SCl_2	SCl	2.00[e]	2.98	564
SbH_3	SbH	1.71[e]	2.35	
SiH_3Cl	SiCl	2.06[e]	2.29	480
SnH_4	SnH	1.70[e]	2.28	1960[b]
$TeBr_2$	TeBr	2.49[e]	1.88	
$TeCl_2$	TeCl	2.36[e]	2.12*	
H_2Te	TeH	1.67[e]	2.68	2300[b]

* After this paper was submitted for publication Dr. H. Sponer called to my attention a recent measurement of the spectrum of $TeCl_2$ by W. Spinnler (Helv. Phys. Acta 18, 297 (1945)), who obtains 2.18×10^5 dynes/cm for the bond-stretching constant.

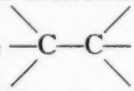
[a] A normal single bond is assumed for each line.

[b] The observed frequency should be about 4 percent lower because of anharmonicity.

[c] L. R. Maxwell, J. Opt. Soc. Am. 30, 374 (1940).

[d] M. T. Rogers, V. Schomaker, and D. P. Stevenson, J. Am. Chem. Soc. 63, 2610 (1941).

[e] Added covalent radii, see reference 4 in text.

relation (IA). It is interesting that k of 4.30 computed from the  valence vibration (1034 cm^{-1}) alone[10] agrees closely with that computed from relation (IA).

Prediction of Some Unknown Force Constants

Table V lists a few molecules to which relation (IA) may be expected to apply. To my knowledge the force constants of these have not been determined from their spectra. Their bond-stretching constants are computed from relation (IA) and are listed in column 5. Vibrational frequencies obtained from these are given in the last column.

In computing the vibrational frequencies the molecules Ge_2H_6 and H_3SiCl were treated as diatomic molecules with the masses of the hydrogen atoms added to the heavier atoms to which they are bonded. The valence force field formula for the bond-stretching frequency, ν_1, of tetrahedral molecules, AB_4, is the simple harmonic formula with the reduced mass, μ_{AB}, being replaced by m_B, the mass of B. This allows a direct calculation of the symmetrical frequency of SnH_4 from k_{SnH} alone. The parallel frequencies, ν_3, of the triatomic molecules, SCl_2 and H_2Te, were computed from the valence force formula[11]

$$\nu_3 = \frac{1}{2\pi}\left[\kappa\left(\frac{1}{m_A}+\frac{1-\cos\alpha}{m_B}\right)\right]^{\frac{1}{2}}$$

assuming the vertex angle α to be 100° in each case. Here m_A and m_B are the masses of the central and end atoms, respectively.

[10] L. G. Bonner, J. Chem. Phys. 5, 293 (1937).

BOND LENGTHS

Table VI compares bond distances calculated from relation (IA) and from Badger's rule[2] with the experimentally observed values. Lengths of other type bonds, computed with Eqs. (IB)–(ID), are listed in Tables II–IV.

Observed Values Used for Comparison

The experimentally observed bond lengths taken from the literature have, on the average, an accuracy of the order of 1 percent. Those for diatomic molecules and for bonds of the polyatomic molecules which are between hydrogen and a heavier atom were with few exceptions determined from measurements of spectra. The probable error for most of them is well below 1 percent. Other bond lengths, determined by electron diffraction, may deviate as much as 1 percent to 3 percent from the correct value.

The values used for IBr and for the C—Se bond of C_2H_6Se are assumed to be the sum of the covalent radii of the bonded atoms. Some of the "observed" d's listed in Table III were, as indicated, determined from the vibrational frequencies by Schomaker and Stevenson[12] using a special form of Badger's rule fitted to the similar molecules Li_2, Na_2, and K_2. These, therefore, do not provide an independent test but merely show that Eq. (IB) agrees closely with Badger's rule for this type of molecule. The fact that the Schomaker-Stevenson rule also agrees closely, except for LiCs, lends credence to these values. As pointed out by Schomaker and Stevenson, the disagreement with their rule by LiCs may indicate an error in ω_e for this molecule.

[11] J. H. Hibben, *The Raman Effect and Its Chemical Applications* (Reinhold Publishing Corporation, New York, 1939), p. 94.

[12] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).

Accuracy of the Relation for Calculation of Bond Lengths

The agreement of the bond lengths calculated from relation (I) with the observed values for the bonds listed in Tables II–IV and VI is almost as good as the accuracy of the observed values. The average deviation of d calculated from d observed for the seventy-one bonds is 1.34 percent. If C_2H_6, CH_3OH, CH_3NH_2, and C_2H_6Se are omitted, the average deviation becomes 1.29 percent for the remaining forty-two molecules of Table IV and 1.18 percent for the sixty-seven remaining ones in all four tables. It will be noticed that the agreement for the molecules of Table IV is hardly as good as that for the molecules in the other tables.

Comparison with Badger's Rule

Though the agreement with the experimentally observed bond lengths, on the average, is markedly better for relation (IA) than for Badger's rule, the advantage is not nearly so great for the computation of bond lengths as for the prediction of force constants. A comparison of the forms of the two relations will reveal why this is true.

The bond lengths and force constants predicted by Badger's rule in Tables I and VI are predominately too small. The average deviation, d calculated from d observed, can be reduced by approximately 1 percent through a different choice of the parameters, c_{ij} and d_{ij}. Apparently Badger selected these parameters to give the best over-all fit for molecules in certain excited states as well as in ground states. The comparisons of Table IV imply that whenever Badger's rule is used with the original c_{ij} and d_{ij} values, the predicted bond lengths should be increased by about 1 percent.

BOND ORDERS

The bond order N as used here represents the effective number of covalent (electron pair) or electrovalent (ionic) bonds acting between the two atoms considered. Bonds like HCl and HF which have partial ionic and partial covalent character[13] are regarded as normal single bonds.

[13] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), Ch. II.

TABLE VI. Observed and calculated bond lengths.

Molecule	Link	Bond lengths in A d obs.	d calc.[a] by Eq. (IA)	Gordy d calc. from d obs. % dev.	d calc. by Badger's rule	Badger d calc. from d obs. % dev.
AsH_3	AsH	1.56[d]	1.57	0.6	1.52	2.6
B_2H_6	BH	1.18[e]	1.21	2.5	1.12	5.1
BeO	BeO	1.331[f]	1.340	.7	1.308	1.7
Br_2	BrBr	2.284[f]	2.317	1.4	2.286	.1
CH_3Br	CBr	1.91[g]	1.86	2.6	1.80	5.8
C_2H_2	CC	1.204[h]	1.206	.2	1.171	2.7
C_2H_4	CC	1.330[i]	1.322	.6	1.255	5.6
C_2H_6	CC	1.55[j]	1.48	4.5	1.43	7.7
CH_3CCH	CC	1.21[k]	1.18	2.5	1.17	3.3
CH_3CCH	C*C	1.46[k]	1.48	1.4	1.39	4.8
C_6H_6	CC	1.39[l]	1.40	.7	1.31	5.8
CH_3Cl	CCl	1.77[g]	1.73	2.3	1.69	4.5
CH_3F	CF	1.396[m]	1.407	.6	1.359	2.7
CH_4	CH	1.093[m]	1.100	.6	1.033	5.5
HCN	C*H	1.057[h]	1.058	.1	1.004	5.0
C_2H_2	C*H	1.057[h]	1.054	.3	1.003	5.1
CH_3NH_2	CN	1.47[n]	1.41	4.1	1.41	4.1
HCN	CN	1.154[h]	1.184	2.6	1.149	.4
H_2CO	CO	1.21[o]	1.19	1.6	1.20	.8
CH_3OH	CO	1.43[p]	1.49	4.2	1.40	2.1
C_2H_6S	CS	1.82[g]	1.82	.0	1.74	4.4
CS_2	CS	1.54[q]	1.53	.6	1.53	.6
C_2H_6Se	CSe	1.94[q]	2.00	3.1	1.84	5.1
Cl_2	ClCl	1.989[f]	2.014	1.3	1.960	1.5
GeH_4	GeH	1.48[r]	1.46	1.3	1.52	2.7
HBr	HBr	1.410[s]	1.397	0.9	1.419	0.6
HCl	HCl	1.275[f]	1.236	3.2	1.299	1.9
HF	HF	.917[f]	.919	.2	.914	.3
HI	HI	1.600[t]	1.603	.2	[c]	
IBr	IBr	2.47[q]	2.50	1.2	[c]	
ICl	ICl	2.321[f]	2.323	.1	2.294	1.2
I_2	II	2.667[f]	2.730	2.4	2.641	1.0
KBr	KBr	2.94[u]	3.18	(8.2)[b]	2.64	(10.2)[b]
KCl	KCl	2.79[u]	3.23	(15.7)[b]	[c]	
KI	KI	3.23[u]	3.17	1.9	[c]	
NaBr	NaBr	2.64[u]	2.71	2.6	[c]	
NaCl	NaCl	2.51[u]	2.51	.0	2.25	10.4
NaI	NaI	2.90[u]	2.81	3.1	2.59	10.7
N_2	NN	1.095[f]	1.082	1.2	1.113	1.6
NH_3	NH	1.014[m]	1.012	.2	.983	3.1
H_2O	OH	.958[m]	.959	.1	.944	1.5
OF_2	OF	1.41[g]	1.37	2.8	1.31	7.1
OCl_2	OCl	1.68[g]	1.65	1.8	1.62	3.6
PH_3	PH	1.45[v]	1.42	2.1	1.41	2.8
H_2S	SH	1.334[w]	1.308	1.9	1.344	.7
H_2Se	SeH	1.53[x]	1.51	1.3	1.47	3.9
H_2S_2	SS	2.05[g]	2.09	1.9	2.03	1.0
SiH_4	SiH	1.45[y]	1.44	.7	1.44	.7
			Average % deviation	1.53	Average % deviation	3.38

* x value for ethylenic C is taken as 2.83.

[a] Force constants used for the calculation are listed in Table I, column 4; bond orders in Table I, column 3; electronegativities in Table VIII, column 3.

[b] Omitted in computing the average deviation.

[c] Badger gives no constants for this combination of period and row of the atomic table.

[d] G. B. B. M. Sutherland, E. Lee, and C. K. Wu, Trans. Faraday Soc. **35**, 1374 (1939).

[e] See reference 43 in text.

[f] See reference 5 in text.

[g] See reference c in Table V.

[h] H. Verleger, Physik. Zeits. **38**, 83 (1937).

[i] E. H. Eyster, J. Chem. Phys. **6**, 580 (1939).

[j] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

[k] L. Pauling, H. D. Springhill, and K. J. Palmer, J. Am. Chem. Soc. **61**, 927 (1939).

[l] V. Schomaker and L. Pauling, J. Am. Chem. Soc. **61**, 1769 (1939).

[m] D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

[n] R. G. Owens and E. F. Barker, J. Chem. Phys. **8**, 229 (1940).

[o] D. P. Stevenson, J. E. LuValle, and V. Schomaker, J. Am. Chem. Soc. **61**, 2922 (1939).

[p] A. Borden and E. F. Barker, J. Chem. Phys. **6**, 553 (1938).

[q] See reference e in Table V.

[r] J. W. Straley, C. H. Tindal, and H. H. Nielsen, Phys. Rev. **62**, 161 (1942).

[s] E. K. Plyler and E. F. Barker, Phys. Rev. **44**, 984 (1933).

[t] A. H. Nielsen and H. H. Nielsen, Phys. Rev. **47**, 585 (1935).

[u] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, Phys. Rev. **52** 968 (1937).

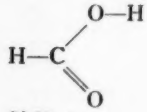
[v] C. C. Stephenson and W. F. Giauque, J. Chem. Phys. **5**, 149 (1937).

[w] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. van Nostrand Company, Inc., New York, 1945), p. 489.

[x] H. H. Nielsen, privately communicated.

[y] G. Herzberg, reference w of Table VI, p. 456.

TABLE VII. Predicted bond orders.

Molecule	Link	Bond-stretching force constants in dynes/cm $\times 10^{-5}$ k obs.	Bond length in A d obs.	Bond order predicted from Eq. (IA) N
BrCN	BrC*	4.2[a]	1.79[a]	1.2
	CN	16.9[a]	1.15[a]	2.7
CH_3CN	CC*	5.3[b]	1.49[c]	1.2
	CN	17.5[b]	1.15[c]	2.8
CH_3NC	CN	5.45[b]	1.43[f]	1.1
	NC	16.3[b]	1.18[f]	2.7
ClCN	ClC*	5.2[a]	1.67[a]	1.3
	CN	16.7[a]	1.15[a]	2.7
	C—O	5.4[c]	1.42[g]	1.0
	C=O	11.8[c]	1.24[g]	1.9
Si_2H_6	SiSi	1.7[d]	2.32[e]	1.2

* x value for acetylenic carbon is taken as 2.83.
[a] See reference 6 in text.
[b] J. W. Linnett, J. Chem. Phys. **8**, 91 (1940).
[c] L. G. Bonner and R. Hofstadter, J. Chem. Phys. **6**, 531 (1938).
[d] T. F. Anderson and A. B. Burg, J. Chem. Phys. **6**, 586 (1938).
[e] See reference *h* of Table VI.
[f] W. Gordy and L. Pauling, J. Am. Chem. Soc. **64**, 2952 (1942).
[g] J. Karle and L. O. Brockway, J. Am. Chem. Soc. **66**, 574 (1944).

Bonds of higher order having some ionic character are treated in a similar manner—i.e., electrovalent and covalent bonds are considered equivalent and additive in assigning the bond orders.

Considering their chemical properties and the valencies of their constituent atoms, the bond orders of most of the molecular links listed in Table I, except those of fractional order, can be assigned with a fair degree of certainty.

Bonds of Fractional Order

Pauling, Brockway, and Beach[14] treat molecules having bonds of fractional order as made up of different resonating structures whose bonds are all of integral order, the bond character being then determined by averaging the integral orders of the bonds between the same pair of atoms in the different contributing structures. Thus the CC bond of benzene would be halfway between a single and a double bond, assuming the two equivalent resonating Kékulé structures to be the only significant ones. Penney[15] has proposed a treatment which, though still based upon the valence-bond method, gives fractional orders which are linearly related to bond energies. For the CC bond of benzene he obtains an order of 1.623.

Coulson,[16] who employs the molecular orbital method, defines the order of a bond in an unsaturated molecule as $1+p$, where the unit value is contributed by the σ electrons which are regarded as localized between the two atoms forming the bond, and where p is the summation of the contribution of all the mobile or unsaturation electrons. He obtains 1.67 for the bond order of the CC benzene bond.

Mulliken, Rieke, and Brown,[17] using the molecular orbital method, have recently shown that hyperconjugation—conjugation with or between saturated groups—has an appreciable effect upon the orders of bonds in hydrocarbons. They predict that normal C—C bonds have about 11 percent double bond character and that normal C=C bonds such as are found in ethylene have about 12 percent triple bond character. For the CC bonds of fractional order in Table I, I have used the bond order values given by these researchers. The agreement of their results with

TABLE VIII. Electronegativities.

Atom	Pauling's[a] value	Value used here	Atom	Pauling's[a] value	Value used here
Ag	—	1.9	K	0.8	0.80
Al	1.5	1.5	Li	1.0	.95
As	2.0	2.0	Mg	1.2	1.2
Au	—	3.1	N	3.0	2.98
B	1.9	1.9	Na	.9	.90
Ba	.9	.9	O	3.5	3.45
Be	1.5	1.45	P	2.1	2.1
Bi	—	1.8	Pb	—	1.5
Br	2.8	2.75	Rb	.8	.78
C	2.5	2.55	S	2.5	2.53
C*	—	2.83	Sb	1.8	1.8
Ca	1.0	1.0	Sc	1.3	—
Cd	—	1.1	Se	2.4	2.4
Cl	3.0	2.97	Si	1.8	1.8
Cs	.7	.75	Sn	1.7	1.7
Cu	—	2.2	Sr	1.0	1.0
F	4.0	3.95	Te	2.1	2.1
Ga	—	1.4	Ti	1.6	1.6
Ge	1.7	1.7	Tl	—	1.3
H	2.1	2.13	Y	1.3	—
Hg	—	1.0	Zn	—	1.2
I	2.4	2.45	Zr	1.6	1.6
In	—	1.4			

[a] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 64.
* Single bond to acetylenic carbon.

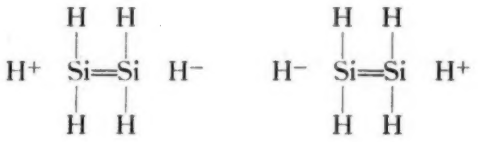
[14] L. Pauling, L. O. Brockway, and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).
[15] W. G. Penney, Proc. Roy. Soc. **158A**, 318 (1937).
[16] C A Coulson, Proc. Roy. Soc. **169A**, 413 (1939); J. E. Lennard-Jones and C. A. Coulson, Trans. Faraday Soc. **35**, 811 (1939).
[17] R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. **63**, 41 (1941).

relation (IA) is pleasing since it lends confirmation to the somewhat surprising hyperconjugation predicted by them. It is unfortunate that bond orders computed by their method are available only for certain CC bonds.

Prediction of Some Bond Orders

Table VII lists several bonds for which stretching constants and interatomic distances are known, but for which bond orders are regarded as uncertain. Relation (IA) is used with the known constants to predict the bond orders listed in column 7. At present there is no check on these other than the method of Pauling, Brockway, and Beach[14] of estimating bond character, which is applicable to some. As is evident from the above discussion, the fractional order predicted by the relation is not strictly equal to the bond character as defined by these authors but is more nearly equivalent to the bond order as computed by Mulliken, Rieke, and Brown.[17]

From its close similarity to ethane, Si_2H_6 may be expected to have some hyperconjugation which would make the order of the SiSi bond somewhat above unity. The order predicted, though not accurate, strongly suggests some double bond character for SiSi. From the electron pair theory the fractional bond order could be explained by postulating structures of the type



to contribute significantly to the ground state.

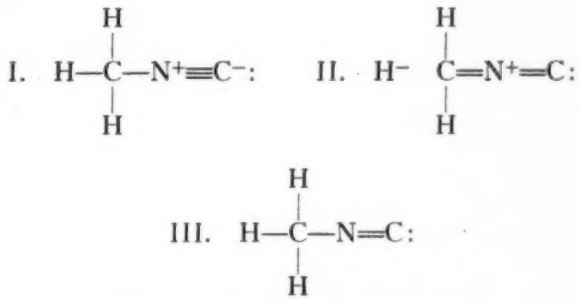
Resonance between structures of the types

giving XC some double bond character, and CN a bond order somewhat less than 3, could explain the bond orders predicted for CH_3CN, ClCN and BrCN. For methyl isocyanide the predicted orders indicate some contribution to the ground state by structures II and III in addition to the principal structure I.

TABLE IX. Calculation of electronegativities.

Molecule AB	Force constant in dynes/cm $\times 10^{-5}$ k obs.[a]	Bond length in A d obs.[b]	Electronegativity from relation (I) x_A	Equation used
AgCl	1.83	2.42	1.76	(IA)
AgBr	1.68	2.59	1.89	(IA)
AgI	1.45	2.81	1.96	(IA)
AuCl	2.56	2.48	3.10	(IA)
AlCl	2.08	2.12	1.53[c]	(IE)
AlBr	1.71	2.29	1.53[c]	(IE)
AlI	1.31	2.50	1.50[c]	(IE)
BCl	3.40	1.77	1.91[c]	(IE)
BBr	2.69	1.94	1.90[c]	(IE)
BiH	1.70	1.809	1.83	(ID)
CdH	1.21	1.762	1.07	(ID)
CuCl	2.29	2.24	2.14	(IA)
CuBr	2.03	2.42	2.24	(IA)
CuI	1.72	2.63	2.28	(IA)
GaCl	1.83	2.11	1.31	(IE)
GaBr	1.52	2.28	1.33	(IE)
GaI	1.24	2.50	1.41	(IE)
HgH	1.14	1.741	.97	(ID)
InCl	1.58	2.29	1.29	(IE)
InBr	1.36	2.46	1.35	(IE)
InI	1.11	2.69	1.44	(IE)
PbH	1.45	1.839	1.51	(ID)
TlCl	1.45	2.31	1.19	(IE)
TlBr	1.26	2.48	1.39	(IE)
TlI	1.07	2.71	1.40	(IE)
TlH	1.15	1.870	1.13	(ID)
ZnH	1.51	1.595	1.20	(ID)

[a] Computed from ω_e values of G. Herzberg, reference 5 in text.
[b] The bond lengths for hydrides are from G. Herzberg, reference 5 in text. For the halogens they are determined from the additivity rule using the Schomaker-Stevenson corrections. See reference 4 in text.
[c] These values are included to demonstrate applicability of Eq. (IE). Pauling gives x values for Al and B as 1.5 and 1.9. See Table VIII.



ELECTRONEGATIVITIES

Electronegativity represents the attraction of an atom for the electrons which bind it in a stable molecule. Mulliken[18] has shown that the average of the first ionization energy and the electron affinity of an element is a measure of this quantity. Though his is a rather straightforward measure, it has not proved applicable to a very large number of elements.

[18] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934); **3**, 573 (1935).

Pauling[19] has derived a more widely applicable method based upon the heats of formation of compounds. He shows empirically that

$$x_A - x_B = 0.208\Delta^{\frac{1}{2}},$$

where x_A and x_B are the electronegativities of the elements A and B; and where Δ, the energy above that expected for a normal covalent bond, expressed here in electron volts, is determined from the bond energy D of the bonds A—B, A—A and B—B, thus,

$$\Delta = D(\text{A—B}) - \tfrac{1}{2}\{D(\text{A—A}) + D(\text{B—B})\},$$

by postulation of the arithmetic mean.[20] Mulliken's values and certain other considerations are used to set the origin of the Pauling scale.

The relation which is the subject of this paper offers a means of determining electronegativity from molecular spectra. The method is widely applicable and appears to be of worthwhile accuracy.

Comparison with Pauling's Values

The electronegativity values used to establish the relation are those of Pauling.[21] When a given element was involved in more than one bond its x value was adjusted to give the best over-all fit to relation (I). The values were extended to the third place where the accuracy of the data justified it. In no instance was it necessary to alter the last significant figure given by Pauling—that is, to change the x value by more than 0.05. This is remarkable, since Pauling's values were determined in a different manner from other bond properties. A comparison is given in Table VIII.

Determination of Some New Values

Relation (I) was used to determine a number of x values not given by Pauling. These are also listed in Table VIII. The molecular constants and particular form of relation (I) used for computing them are shown in Table IX.

The only molecules involving Ga and In for which force constants are available are certain diatomic halides. These have unsatisfied valencies which make relation (IA) inapplicable, and their interatomic distances have not been measured. Consequently, I have chosen the parameters a and b of relation (I) so as to give the best fit for the similar halides of B and Al (elements of the same valence) with all interatomic distances determined from the Schomaker-Stevenson rule,[12] and have used the resulting equation,

$$k = 2.25(x_A x_B/d^2)^{\frac{3}{4}} - 0.20, \qquad \text{(IE)}$$

to determine the x values for Ga, In, and Tl. The consistency of the results (see Table IX) appears to justify the procedure.

The x values for Ag and Cu and especially that for Au seem rather high in comparison to those of other metals. The extrapolation of Eq. (IA) to these elements is certainly questionable. Some double bond character may exist in the halides used, and the bond lengths which were determined from the additivity rule[12] may not be sufficiently accurate. Nevertheless, the x values for Ag obtained from three different halides agree reasonably well. The results are likewise consistent for Cu. Values determined from the hydrides were not used in assigning x for these elements because their polyvalent character makes it uncertain which form of the relation applies. However, it seems that the correct values should be somewhere between those given by Eqs. (IC) and (ID): 1.6 and 2.1 for Ag, 1.7 and 2.3 for Cu, 3.0 and 3.9 for Au. The values assigned are in qualitative agreement with other properties.[22] Elements of sub-group I —Cu, Ag, and Au—have much higher ionization potentials, higher boiling points, form oxides that are less basic, etc., than do elements of the main group I—Li, Na, etc.

Effects of Bond Type

Carbon bound by a triple and a single bond shows a significantly higher electronegativity in the direction of the single bond than does carbon held by bonds of lower order. Possible causes of this are the less effective shielding of the nucleus by the electrons involved in the triple bond and the smaller than normal[23] single bond radius which allows a closer approach of the bonding

[19] L. Pauling, reference 13, p. 58.
[20] L. Pauling, reference 13, p. 48.
[21] L. Pauling, reference 13, p. 64.
[22] W. M. Latimer and J. H. Hildebrand, *Reference Book of Inorganic Chemistry* (The Macmillan Company, New York, 1940), p. 101.
[23] L. Pauling, H. D. Springhill, and K. J. Palmer, J. Am. Chem. Soc. 61, 927 (1939).

electrons to the nucleus. This higher value of x in ≡C— is revealed in other phenomena. Hydrogens joined to acetylenic carbon are known to be more acidic[24] and to participate in hydrogen bonding more effectively than do those of a more saturated hydrocarbon.[25] In this work the x value for ≡C— was chosen which provided the best fit for the CH bond of HCN and of C_2H_2, and this value was used for other single bonds to a triple bonded carbon.

Other variations in bond character—bond type, degree of hybridization of the atomic orbitals—no doubt influence the effective electronegativities. Their effects, which do not seem as pronounced as that of acetylenic C, are neglected.

Effects of Electric Charges

The x values listed in Table VIII do not hold for charged atoms. However, Pauling[26] has given simple rules, based on changes in nuclear screening, for correcting these values for the effects of electric charges. If x^+ represents the electronegativity of an element with a +1 charge, then

$$x^+ = x + \tfrac{2}{3}(x_r - x)$$

approximately, where x is the value for the neutral atom and x_r is the value for the atom immediately to the right of it in the atomic table. Similarly for a negative unit charge,

$$x^- = x - \tfrac{2}{3}(x - x_l),$$

where x_l is the electronegativity of the element immediately to the left in the atomic table. These rules are used to correct for the effects of formal charges in ionic groups treated in this paper.

For most applications of relation (I), the effects of partial ionic character of a bond on the x values may be neglected as the electronegativity product tends to remain constant when the x value of one of the bonded atoms is increased at the expense of the other.

SPECIAL APPLICATIONS

$(MH)^+$

Assuming a normal bond order of unity for these ions, higher force constants would be predicted for them, because of their greater electronegativity product, than for the corresponding neutral group. When M^+ has a large x value compared to H, however, contributions of the form, M H^+, with zero bond order, could reduce the bond order enough to more than counterbalance the effects of the greater electronegativity product. Thus, understandably, force constants for $(HCl)^+$ and $(OH)^+$ are lower than those of the corresponding neutral group, whereas those for $(BH)^+$ and $(BeH)^+$ are higher.

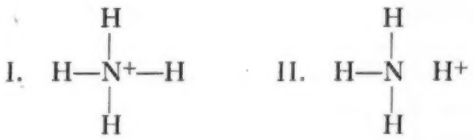
From relation (I), the bond order of M^+—H is approximately

$$N' = (k'/k)(x_M d'^2/x_M' d^2)^{\frac{1}{4}},$$

where the primed constants are for M^+—H. This assumes that a and b have the same value for M—H and M^+—H and that b is small compared to k or k'. The former assumption is certainly questionable in some instances, and the computed N's should be regarded as only approximate predictions. The bond orders for $(OH)^+$, $(HCl)^+$, $(BH)^+$, and $(BeH)^+$ computed in this way, using Herzberg's[5] constants, are 0.6, 0.8, 0.9, and 1.0, respectively.

$(NH_4)^+$ and $(H_3O)^+$

The principal structures contributing to the ground state of $(NH_4)^+$ would be I and the four equivalent forms of II.



Pauling[27] has predicted 20 percent ionic character for NH. I shall assume equal resonance between I and each of the forms of II. This would mean that a particular NH is bonded only 80 percent of the time—since no effective bond exists in N H$^+$—and that N = $\frac{4}{5}$. The x value of N is increased by about .1 since it has a + charge $\frac{1}{4}$ of the time that a given NH is bonded. The NH distance will not be greatly different from that in NH_3, and I shall take it to be 1.02A. With these assumptions relation (IA) gives $k_{NH} = 5.64$. If this value is decreased 8 percent to correct for anharmonicity and the simple har-

[24] J. B. Conant and G. W. Wheland, J. Am. Chem. Soc. **54**, 1212 (1932).
[25] S. C. Stanford and W. Gordy, J. Am. Chem. Soc. **63**, 1094 (1941).
[26] L. Pauling, reference 13, p. 65.
[27] L. Pauling, reference 13, p. 72.

monic formula applied, the predicted vibration frequency is 3070 cm^{-1}. This is in good agreement with the absorption of the ammonium halides[28] in the region of 3100, which presumably arises from the valence vibration of $(NH_4)^+$.

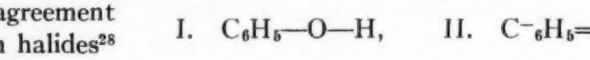
A similar treatment can be given $(H_3O)^+$. Assuming equal resonance between I and each of the three equivalent forms of type II,

the bond order is effectively $\frac{3}{4}$, and the average electronegativity of O is increased about 0.1 by the + charge. With $d_{OH}=0.97$, the estimated k_{OH} is 5.96. The ion should absorb in the region of 3120 cm^{-1} or 3.2μ. This, as it should be, is a little beyond the position to which the H_2O band is shifted by the strong hydrogen bonds existing in pure water. These ions would exist in a solution of a strong acid in water, but it would hardly be possible to resolve their absorption from that of liquid water and ions of the type $(H_4O)^{++}$. A strong acid should, however, tend to broaden the 3μ water band on the long wavelength side.

CH-NH_2, CH_3OH, C_6H_5OH, and C_6H_5SH

Linnett[29] regards the NH and OH stretching force constants which he computes for these compounds as lower than normal. If his values for methyl amine and methyl alcohol, 6.30 and 7.65, respectively, are increased 8 percent to correct for probable effects of anharmonicity, the resulting values, 6.80 and 8.26, are in almost exact agreement with the values 6.81 and 8.24 computed from relation (IA) assuming normal single bonds.

The OH stretching constant obtained by Linnett for phenol does, however, appear to be significantly lower than that for water or for methyl alcohol. Phenol[30] is known to be appreciably more acidic than the aliphatic alcohols. Pauling[31] attributes this to structures of Type II in resonance with those of Type I.



The OH bond order predicted by relation (IA) is 5 percent lower than unity. Hence, it appears that structures of Type III are also of importance.

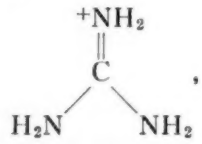
Linnett's value for the SH bond-stretching constant of thiophenol 3.8 (or for CH_3SH) after the estimated correction for anharmonicity is made becomes 4.1, the value predicted for a normal SH bond by relation (IA).

C⁻≡N

The force constant of C⁻≡N computed from the CN vibrational frequency of NaCN[32] is 16.5, a value somewhat lower than that for the CN group of HCN. The lower force constants for the ion can be accounted for without assuming any decrease in the bond order, by decreasing the x of C by 0.3 and increasing the bond distance by 0.05A to correct for the negative charge[33] on C. The value predicted in this way from relation (IA), assuming a triple bond, is 16.2, in excellent agreement with the observed value.

Guanidonium Ion

According to Pauling[34] the guanidonium ion resonates equally between the equivalent structures of the type,

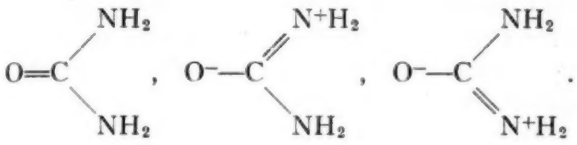


giving the CN bond 33 percent double bond character. Assuming N=1.33, and using the $k_{CN}=7.1$ computed by Kellner,[35] the CN distance calculated from (IA) is 1.34A. This seems to be a reasonable value. Pauling's relation[36] between bond distance and double bond character, assuming 33 percent double bond character, gives $d_{CN}=1.36$A.

[28] J. H. Hibben, reference 11, p. 466.
[29] J. W. Linnett, Trans. Faraday Soc. **91**, 223 (1945). The value given is increased by 8 percent to correct for anharmonicity.
[30] H. J. Lucas, *Organic Chemistry* (American Book Company, New York, 1935), p. 131.
[31] L. Pauling, reference 13, p. 189.
[32] W. Gordy and D. Williams, J. Chem. Phys. **3**, 664 (1935).
[33] L. Pauling, reference 13, p. 159.
[34] L. Pauling, reference 13, p. 198.
[35] L. Kellner, Proc. Roy. Soc. **177**, 456 (1941).
[36] L. Pauling, reference 13, p. 164.

Urea

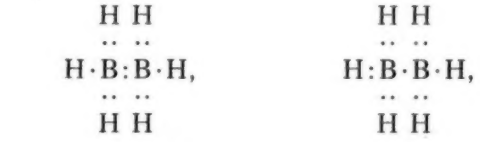
The principal structures contributing to the ground state of urea are:



Kellner[35] has computed from spectra $k_{CO}=9.7$ and $k_{CN}=6.6$. Using these values and the interatomic distance values $d_{CO}=1.25$A and $d_{CN}=1.37$A, measured by Wyckoff and Corey,[37] the bond orders obtained from (IA) are 1.5 and 1.3 for CO and CN, respectively. Pauling[34] predicts 20 percent double bond character for CN and 60 percent double bond character for CO.

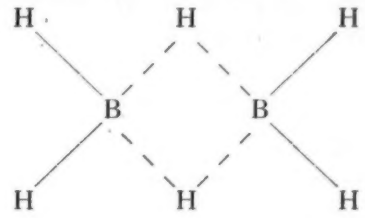
B_2H_6

Because of its unusual and still somewhat uncertain structure this molecule is of great interest. Lewis[38] has suggested that the total of twelve valence electrons available combines into six electron pair bonds which resonate among the seven bonds to give 6/7 of a normal electron pair bond for each. Pauling[39] assumes that in resonance with these are several structures of the type,



containing one-electron bonds. Since a one-electron bond is approximately equivalent to one-half an electron-pair bond, each of the bonds would still average about 6/7 of a normal single bond. Taking $N=6/7$ for BH and BB and the bond distances measured by Bauer,[40] $d_{BH}=1.27$A, $d_{BB}=1.86$A, the force constants computed from relation (IA) are $k_{BH}=3.1$ and $k_{BB}=1.8$. This value of k_{BH} does not agree satisfactorily with that of 3.9 computed from the observed spectra.[29,41] The B—B vibrational band for $k_{BB}=1.8$ should occur at about 660 cm^{-1}. No very strong band is observed near this frequency in either the Raman or infra-red spectra.[42]

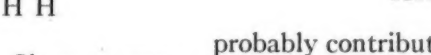
Recently Longuet-Higgens and Bell[43] have proposed the bridged structure

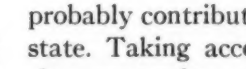


held together with hydrogen bridges, with no direct bonding between the borons and with normal single bonds between the terminal BH groups. Relation (IA) supports their interpretation. Using their value, 1.18A for the B—H distance, and assuming a normal single bond, N=1, the B—H force constant computed from (IA) agrees closely with that computed by Linnett[29] from the data of Stitt.[42] See Table I.

CO_2, SCO, and CS_2

Normal electronic structures with double bonded links can be assigned to carbon dioxide. Nevertheless, the CO distance, 1.16A, is somewhat shorter than that for a double bond, and Pauling[44] has shown that the three structures,





probably contribute about equally to the ground state. Taking account of the effects of formal charges on the x value of O and of the triple bond on the x of C for the second two structures in proportion to their contribution and with N equal to the average bond character (2.00), the bond-stretching constant from (IA) is 14.4. This is in fair agreement with the observed value,[6]

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[37] R. W. G. Wyckoff and R. B. Corey, Zeits. f. Krist. **89**, 462 (1932).

[38] G. N. Lewis, J. Chem. Phys. **1**, 17 (1933).

[39] L. Pauling, reference 13, p. 241.

[40] S. H. Bauer, J. Am. Chem. Soc. **59**, 1096 (1937).

[41] Anderson and Burg (reference d of Table VII) tentatively assigned the widely separated frequencies 2102 cm^{-1} and 2523 cm^{-1} both to a BH_2 stretching vibration, offering resonance splitting as a possible cause of the separation. From this questionable assignment they obtained a value of 3.0 for k_{BH}. They point out, however, that the separation of 421 cm^{-1} is abnormally large for resonance splitting.

[42] F. Stitt, J. Chem. Phys. **9**, 780 (1941). See also reference d of Table VII.

[43] H. C. Longuet-Higgens and R. P. Bell, J. Chem. Soc. 250 (1943).

[44] L. Pauling, reference 13, p. 179.

15.2. A similar interpretation can be given for SCO.

The resonance energy of CS_2, only 11 kcal./mole[45] as compared with 33 kcal./mole for CO_2, indicates that structures of Types II and III are much less significant in this molecule. I have consequently regarded it as having normal double bonds. See Table I.

O_2, SO, and S_2

One might expect, from their covalencies, two normal electron-pair bonds in these molecules. Their $^3\Sigma$ ground states,[5] nevertheless, indicate that they have unpaired valence electrons. Pauling[46] has postulated for them a normal single bond plus two three-electron bonds. Though the two three-electron bonds in these molecules should be about equal in energy to a single bond,[46] it is not possible to regard their bond order as 2.00 in the present relation. The bond orders required to make the relation fit are 1.4, 1.7, and 1.9 for O_2, SO, and S_2, respectively. Se_2 and Te_2 behave similarly.

PN and P_2

The force constant calculated from (IA), assuming triple bonds for these molecules, is too large by 8 percent for PN and by 10 percent for P_2. It is not probable that these deviations are caused by errors in the observed k's or d's, which are those listed by Herzberg.[5] They could be made to fit the relation adequately by an 8 percent reduction in the x value for P. However, the x used for P seems to be satisfactory for PH_3. There is no apparent reason why these molecules should be exceptions to the relation since the similar molecule N_2 is not an exception. PN and P_2 are usually regarded as having pure triple bonds. The tendency to form triple bonds, however, decreases rapidly with the increase in size of the atoms bonded, and tentatively I am attributing the misfit of the relation to this tendency.

The necessary reduction in bond order may be achieved in these molecules by a small contribution from structure II, containing a single bond and incompleted octets on both atoms.

I. :P:::P: , II. $\overset{\cdot\cdot}{:}\overset{\cdot\cdot}{P}:P:$.

The incompletely-filled valence shells should allow the second structure to exist with the same interatomic distance as that required by I, though because of its much higher energy the contribution from II may not be very significant.

H_2O_2 and H_4N_2

In contrast to the satisfactory agreement of the similar molecules H_2S_2 and H_6C_2, both H_2O_2 and H_4N_2 appear to be exceptions to relation (IA). This behavior will be treated in a later communication.

Pyramidal AB_3 Molecules

When A is not large compared to B, these molecules are complicated by the possibility of interaction of the non-bonded atoms. The radius ratio r_A/r_B should give a relative indication of this interaction. Consequently, I have listed the molecules in Table X in the order of increasing values of r_A/r_B. From an examination of the table it is seen that the bond-stretching force constants calculated from (IA), assuming normal single bonds, agree satisfactorily with the observed values for all molecules with r_A/r_B greater than 1.5. For those with r_A/r_B between 1.2 and 1.5 the agreement is fair except for $BiCl_3$. The exceptional disagreement for $BiCl_3$ makes the observed k appear questionable.

No observed k's are available for the iodides. Because of the large radius of iodine the radius ratio would be unfavorable to a good fit of (IA) for them.

Bond-stretching constants predicted from (IA) for $SbBr_3$ and $BiBr_3$ (radius ratios 1.24 and 1.28) are 1.71 and 1.59, respectively.

Tetrahedral AB_4 Molecules

Except when B is the small hydrogen atom, there is considerable interaction between the non-bonded corner atoms of AB_4 tetrahedral molecules. The valence force function is in general unsatisfactory for this type of molecule. For some of them Urey and Bradley[47] and

[45] L. Pauling, reference 13, p. 131.
[46] L. Pauling, reference 13, pp. 253–4.
[47] H. C. Urey and C. A. Bradley, Phys. Rev. **38**, 1969 (1931).

TABLE X. Calculated and observed bond-stretching force constants for pyramidal AB_3 type molecules.

Molecule	Bond length in A d obs.[a]	Bond-stretching force constants in dynes/cm $\times 10^{-5}$ k obs.	k calc.[b] by Eq. (IA)	k calc. from k obs. % dev.	Radius ratio r_A/r_B
AsH_3	1.56	2.81[c]	2.84	1.1	3.32
PH_3	1.45	3.33[c]	3.24	2.7	2.98
NH_3	1.014	6.86[c]	6.81	.7	2.00
$Bi(CH_3)_3$	2.23	1.75[d]	1.87	6.9	1.90
$Sb(CH_3)_3$	(2.13)	2.09	1.99	4.8	1.83
AsF_3	1.72	3.92[e]	3.79	3.4	1.75
$As(CH_3)_3$	1.98	2.44[d]	2.34	4.1	1.63
PF_3	1.52	4.59[e]	4.66	1.5	1.56
$BiCl_3$	2.48	1.19[e]	1.80	(51.0)	1.48
$SbCl_3$	2.37	1.78[e]	1.91	7.3	1.43
$P(CH_3)_3$	1.87	2.14[d]	2.60	21.5	1.43
$AsCl_3$	2.16	2.03[e]	2.30	14.8	1.27
PCl_3	2.00	2.12[e]	2.63	24.0	1.11
$N(CH_3)_3$	1.47	3.97[d]	4.58	15.4	.96
PBr_3	2.23	1.63[e]	2.17	33.2	.96

[a] The hydrides are repeated from Table I. Bond distances for other molecules are from reference c of Table V except those in parentheses, which are the added radii.
[b] Normal single bonds are assumed.
[c] See reference e of Table I.
[d] J. E. Rosembaum, D. J. Ruben, and C. R. Sandberg, J. Chem. Phys. 8, 366 (1940).
[e] G. Herzberg, see reference w of Table VI, p. 456.

others[48] have successfully used modified valence potential functions with terms included to account for the interaction of the corner atoms.

Herzberg[49] and Silver[50] have computed bond-stretching constants for several tetrahedral type molecules assuming the simple valence force system. These values do not agree with those computed from (IA) but agree, except when A is carbon, with values computed from relation I in the form,

$$k = 3.29\left(\frac{x_A x_B}{d^2}\right)^{\frac{3}{4}} - 0.40. \qquad \text{(IF)}$$

The results of this comparison are shown in Table XI. They imply that the interaction of the non-bonded atoms varies in a systematic manner for the different types listed. An equally satisfactory fit is obtained for the series CF_4, CCl_4, CBr_4, and $C(CH_3)_4$ if the constants a and b of relation (I) are given the values $+2.94$ and -1.40.

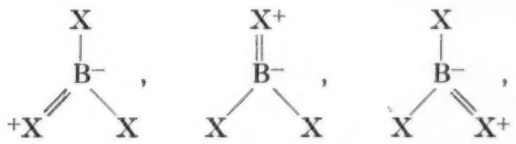
A force stretching the bond AB in these molecules would be opposed not only by the chemical binding of AB but also by components of the interaction forces of the corner atoms.

[48] N. S. N. Nath, Ind. J. Phys. 8, 581 (1934). See also K. W. F. Kohlrausch, reference r of Table I, p. 157.
[49] G. Herzberg, reference w of Table VI, p. 182.
[50] S. Silver, J. Chem. Phys. 8, 919 (1940).

Thus quite understandably the AB stretching constants computed from (IA), assuming only the forces of a normal single bond, are lower than those obtained from spectra using the valence force field system. An additional factor tending to make the values from (IA) (with $N = 1.00$) lower than the spectral constants is the probable existence[51] of some double bond character in the bond AB.

Boron Halides

The boron halides are symmetrical planar molecules with bond distances considerably shorter than those expected for normal single bonds. Pauling[52] has predicted the three equivalent structures of type,



to be the principal ones contributing to their ground states. Neglecting all structures except the above type and counting in the ionic bond, the average bond character is 5/3. Applying relation (IA) with $N = 5/3$ gives $k = 4.06$, 4.77, and 8.80 for BBr_3, BCl_3, and BF_3 in this order. Assuming the valence force system, which holds reasonably well for these molecules, Herzberg[53] computes from their spectra 3.66, 4.63, and 8.83 for k_{BBr}, k_{BCl}, and k_{BF}, respectively.

SOME GENERAL DEDUCTIONS

1

If the bond order remains unchanged, a formal positive charge on one of the atoms of a bond should increase its stretching force constant, and a negative formal charge should decrease it. This follows from the fact that an increased positive charge on either atom would increase the electronegativity product and would also—unless the bond order is lowered—tend to make the bond length shorter.

The implication of the above statement is that when, as frequently happens,[29] a positive

[51] L. Pauling, reference 13, Ch. VII.
[52] L. Pauling, reference 13, p. 219.
[53] G. Gerzberg, reference w of Table VI, p. 178.

charge actually lowers the force constant, it also effectively reduces the bond order. That a decrease in the electron density of one of the bonded atoms would tend to reduce the bond order is not surprising. For illustrations, see the sections on $(MH)^+$ and $(NH_4)^+$.

2

For bonds of different orders between the same pair of atoms the force constant k_m for any given bond order N_m is related to that k_n for some other order N_n by

$$\frac{k_m-0.30}{k_n-0.30}=\frac{N_m}{N_n}\left(\frac{d_n}{d_m}\right)^{\frac{1}{3}}.$$

This follows obviously from relation (IA). More approximately,

$$\frac{k_m}{k_n}=\frac{N_m}{N_n}\left(\frac{d_n}{d_m}\right)^{\frac{1}{3}}.$$

In the above equations d_m and d_n represent the interatomic distances for the respective bond orders, N_m and N_n.

Frequently it is desirable to know the approximate ratios of the force constants of single, double, and triple bonds between a given pair of atoms. If the interatomic distances have not been measured for the different bonds, they can be determined approximately by adding the respective single, double, or triple covalent radii given by Pauling.[54] Whenever k is known for one of the orders, the first and more accurate of the above forms can be applied. Thus the bond-stretching force constants for single, double, and triple CN bonds should have the approximate ratios, 1.00:2.37:4.10. Probably a more useful application is the prediction of bond orders from force constant ratios.

[54] L. Pauling, reference 13, p. 154.

TABLE XI. Calculated and observed bond-stretching force constants for tetrahedral AB_4 type molecules.

Molecule	Bond length in A d obs.[a]	Bond-stretching force constant in dynes/cm $\times 10^{-5}$ k obs.[b]	k calc. from Eq. (IF)	k calc. from k obs. % dev.
$GeBr_4$	2.32	2.58	2.56	0.8
$GeCl_4$	2.08	3.27	3.28	.3
$SiBr_4$	2.19	2.92	2.94	.8
$SiCl_4$	2.02	3.75	3.63	3.2
$Si(CH_3)_4$	1.93	3.31	3.45	4.2
SiF_4	1.54	7.16	7.10	.8
$SnBr_4$	2.45	2.28	2.32	1.8
$SnCl_4$	2.30	2.80	2.77	1.1
$TiCl_4$	2.21	3.11	2.82	9.3

[a] SiBr distance in $SiBr_4$ is assumed to be equal to that in $SiBrCl_3$; SnBr distance is determined from the Schomaker-Stevenson rule, reference 4. Other distances are from Maxwell, reference *c* of Table V.
[b] k for $Si(CH_3)_3$ is from Silver, reference 50. k's for the other molecules are from G. Herzberg, reference 49.

3

The concept of electronegativity, which in the past has been used principally in predicting properties associated with the partial ionic character of bonds, is of real importance in the interpretation of molecular spectra. Previous applications have been primarily concerned with the quantity, x_A-x_B, a fact which apparently led Wheland[55] to comment that it is only the differences between electronegativities which are significant. In the present work, wide application has been made of the electronegativity product, x_Ax_B.

I wish to thank Vida Miller Gordy for assisting with the calculations and the preparation of the manuscript.

[55] G. W. Wheland, *The Theory of Resonance* (John Wiley & Sons, Inc., New York, 1944), p. 84.

The Thermodynamic Properties and Potential Energy of Solid Argon. II

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In the first paper with this title, a relation was derived from the available experimental data giving the Debye characteristic temperature of solid argon as a function of a (the interatomic distance) or V (the molal volume of the solid). This relation was not consistent with the usual Grüneisen assumption, which for a small range of volumes may be written approximately $-\Theta^{-1}d\Theta/dV=$constant. In this paper it is shown that the Grüneisen assumption, with the constant set equal to 0.18 mole cc^{-1} is reasonably consistent with the experimental data. On this basis a new relation between the potential energy E_p of solid argon and a is derived. Most of the earlier conclusions are unaltered, but the present basis seems more reasonable, and, as will be shown in the following paper, avoids difficulties when application is made to liquid argon.

IN a paper of the same title[1] (referred to hereinafter as I) we have used the available thermal and equation-of-state data on solid argon to determine the potential energy, E_p, and the Debye characteristic temperature, Θ, of the solid as functions of a, the equilibrium distance between nearest neighbors in the lattice. The relation thus obtained between Θ and a has the peculiarity that $d\Theta/da$ varies extremely rapidly with a. In fact, it gives $d\Theta/da=-211$ degree per angstrom at $a=3.86$A (with Θ itself, of the order of 80°), and $d\Theta/da=0$ at $a=3.924$A. This rapid variation seems extremely improbable, and when an attempt is made to apply such a function to a study of liquid argon it leads to difficulties. To be sure, the experimental data on which our expression for Θ was based extend only over a range of a from about 3.82 to 3.86A, so that anything outside this range may be said to be an extrapolation; however, even in this range, $-d\Theta/da$ varied from about 273 to 211. It appears quite possible that this apparent, rather violent variation of $d\Theta/da$ may be due to experimental error. In fact, as explained in the following article,[2] an examination of Bridgman's data[3] indicates that they do not conform exactly to the values given by him for the volume of the liquid in equilibrium with the solid at various temperatures, and a new set of values has been estimated. These give rise to new values for the volume of the solid in equilibrium with the liquid, which differ appreciably from those given by Bridgman.

Since our work was based on these volumes, some alteration in the results is obviously indicated, and it also appears that the margin of error may be somewhat greater than previously assumed. It, therefore, now appears reasonable to try the simple Grüneisen assumption,

$$d\ln\Theta/d\ln V=\text{constant},$$

where V is the molal volume; actually, since our range of V is small, and it is just as good theoretically and much more convenient, we set

$$-\Theta^{-1}d\Theta/dV=\Gamma, \qquad (1)$$

where Γ is a constant. This is also nearly equivalent to setting $d\Theta/da$ constant, in view of the small range of a and Θ involved, and so in this respect the behavior of Θ is quite different from that supposed previously. The definition of the functional dependence of Θ is completed by setting

$$\Theta=70.56° \text{ at } V=24.493 \text{ cc/mole} \quad (a=3.8600\text{A}). \qquad (2)$$

These equations replace Eq. (6) of I. Such a relationship must have an empirical basis, and can be considered as satisfactory only if it is consistent with the experimental data. To test this consistency we make use of Eq. (5) of I, which may be rewritten in the form

$$-P=\Theta^{-1}(d\Theta/dV)[(E_t+E_z)-(E_t+E_z)_{P=0}]. \qquad (3)$$

[1] O. K. Rice, J. Chem. Phys. **12**, 289 (1944). *Erratum*: Sign inside bracket on right-hand side of Eq. (4) should be + instead of −.
[2] O. K. Rice, J. Chem. Phys. **14**, 324 (1946).
[3] P. W. Bridgman, Proc. Am. Acad. **70**, 1 (1935).

TABLE I. Test of relation between Θ and V.

T °K	P cal./cc	V(obs.), cc/mole Bridgman	V(obs.), cc/mole Revised	Θ(calc.) $\Gamma=0.18$	V(calc.) $\Gamma=0.18$	Θ(calc.) $\Gamma=0.195$	V(calc.) $\Gamma=0.195$
83.78	0	24.50†	24.50†	70.62*	24.489	70.62*	24.489
126.3	46.9	24.49	24.43	71.31	24.434	70.24	24.516
161.9	93.7	24.37	24.17	73.86	24.239	71.88	24.398
192.9	140.6	24.25	24.01	77.12	23.999	74.66	24.203

* Calculated from Table I of I.
† From Baly and Donnan; see reference 4.

In this equation P is the pressure at any given value of V and of the temperature, T, and E_t and E_z in the first parenthesis are the thermal and zero-point energies at this V and this temperature, while in the second parenthesis they are evaluated at the same value of V but at zero pressure and whatever temperature corresponds thereto.

To make use of Eq. (3) we note, first, that Table I of I gives an empirical relation between $(E_t+E_z)_{P=0}$ and Θ, both of which are determined there directly from the experimental data. On the other hand, the value of E_t+E_z can be obtained from the Debye theory as a function of Θ/T. These two relations, together with Eq. (1), enable us to express the pressure P at any given T as a function of Θ, and, hence, through Eq. (1), as a function of V (or its equivalent a). The result of this procedure is thus to give a relationship between P, V, and T, which can be used to calculate V for the solid at values of P and T corresponding to various points along the melting curve. These calculated V's can then be compared with those given by Bridgman or with our revised values. The results are given[4] in Table I. It will be seen that calculations of V based on $\Gamma=0.195$ agree well with Bridgman's original estimates of V, while calculations based on $\Gamma=0.18$ agree well with my revised values. Accepting the latter, it is clear that the results obtained by the use of $\Gamma=0.18$ are certainly well within the limits of experimental error. It may seem surprising that, by fitting Bridgman's V exactly as we did in I, we obtained results so different with respect to the behavior of $d\Theta/dV$, but this happens because all the other properties are very sensitive to small changes in the volume. On the other hand, experimental measurements of the volume are not correspondingly highly accurate, so that the representation given by Eq. (1) appears to be quite adequate.

The agreement with the measurement of $(\partial P/\partial T)_V$ at 73°K and zero pressure, made by Simon and Kippert[5] is scarcely altered as compared with that in I. Calculating $(\partial P/\partial T)_V$ from the relation

$$(\partial P/\partial T)_V=-\Theta^{-1}(d\Theta/dV)C_v=\Gamma C_v, \qquad (4)$$

(see Eq. (7) of I), using $\Gamma=0.18$, we find $(\partial P/\partial T)_V=42$ atmos./deg.; in I it was evaluated as 43 atmos./deg. The experimental value is 38 atmos./deg.

In spite of the differences between Eq. (1) of the present article and Eq. (6) of I, the conclusions drawn in the earlier work are not substantially modified. In the experimental range of volumes involved in Bridgman's measurements of the solid, $-\Theta^{-1}d\Theta/dV$ as calculated from I, ranges from 0.157 to 0.193, of the same order of magnitude as the 0.18 found here.[6] On the other hand, the calculations of my earlier article[7] in which an attempt was made to establish a theoretical connection between Θ and E_p, made it appear that $-\Theta^{-1}d\Theta/dV$ could

[4] The values of a given in Table II of I were slightly altered from those calculated directly from the values of V given by Bridgman, because the estimated value $V=0.616$ cc/g (see end p. 291 and top p. 292 of I) does not correspond exactly to the value of a at the melting point obtained from Table I of I. In Table I of the present paper the values of V(obs.), Bridgman, at the higher temperatures correspond exactly to those given by Bridgman, but the value at 83.78° is obtained from the measurements of the density of the liquid by E. C. C. Baly and F. G. Donnan (J. Chem. Soc. London **81**, 907 (1902)), and the measurement of ΔV of fusion by K. Clusius and K. Weigand (Zeits. f. physik. Chemie **B46**, 1 (1940)). Bridgman's value of ΔV of fusion at 83.78 is probably in error, but his value of the density of the liquid is close to that of Baly and Donnan.

[5] F. Simon and F. Kippert, Zeits. f. physik. Chemie **135**, 113 (1928).

[6] This means that the total expansion of the solid between 0°K and the melting point is scarcely changed from that shown in Table I of I.

[7] O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941).

not be greater than about 0.10 in the experimental range, which is a very significant difference. It was already pointed out in this earlier article that these results were not consistent with the work of Simon and Kippert, nor are they consistent with Bridgman's data.

In I it was concluded that the previously derived[7] theoretical relation between Θ and E_p probably was not valid because the vibration of an atom in the fields of its neighbors would be markedly anharmonic, even when only zero-point vibrations were involved. This situation arose because the curvature of the E_p *vs.* a curve changed rapidly. This conclusion is not invalidated by the results of the present paper, when they are combined with Table I of I, to give a new relation between E_p and a.

The direct method of getting this relationship would be to use Eqs. (1) and (2) above to get V, and hence a, as a function of Θ. In this way we could assign new values for a for the temperatures in Table I of I, and so obtain a new relation between E_p and a. However, in the course of some other calculations being made in collaboration with Mr. G. W. Murphy, it appeared that a much more accurate relation could be obtained by an indirect method, using the Grüneisen equation for the pressure [Eq. (3) of I]. For the special case of zero pressure, this equation becomes

$$0=\Gamma(E_t+E_z)-dE_p/dV. \tag{5}$$

From Table I of I, we can find E_t+E_z as a function of Θ. The following empirical equation expresses this relationship quite well:

$$E_z+E_t=296.7+29.5(80-\Theta)-0.643(80-\Theta)^2. \tag{6}$$

Eq. (6) comes directly from the experimental data and the Debye theory, and is not affected by the dependence of Θ on a. With any given value of Γ, however, it can be changed into a relation between E_z+E_t and a, and inserted into Eq. (5); at the same time dV may be expressed in terms of da. We then obtain dE_p/da as a function of a. It is convenient to set up a new empirical expression for dE_p/da. This has been done, and it has been integrated to give

$$-E_p=2007.6-1410.0x-10{,}710x^2+53{,}947x^3-76{,}500x^4, \tag{7}$$

where $x=a-3.84$. The greater accuracy of this method of obtaining the expression for E_p arises because the absolute error of E_z+E_t in Table I of I is about the same as that of E_p. Small but changing errors in E_p can make appreciable differences in dE_p/da; on the other hand, such small errors are a very small percentage of E_z+E_t which can, therefore, be used in Eq. (5) to get a much more accurate value of dE_p/da. This, when integrated, using an integration constant to match E_p in Table I of I at one value of Θ (correlated with x from Eqs. (1) and (2)), should give a better expression for E_p than that obtained directly.

We may now compare Eq. (7) above with Eq. (8) of I. The coefficients of x^3 and x^4 in Eq. (7) are much smaller than the corresponding ones of Eq. (8) of I, while the coefficient of x^2, with which the other coefficients must be compared, is larger. Nevertheless, the rate of change of curvature of Eq. (7) is still quite substantial. Thus the value of d^2E_p/da^2 obtained from Eq. (7) changes by about 150 percent in a range of a of about 0.1A. However, this estimate is based on the third-degree term in the expression for E_p, and when we consider the motion of an atom surrounded by a highly symmetrical distribution of neighbors, the effects of any term of odd order, in causing anharmonicities in the effective field in which the atom vibrates, tend to cancel out in first approximation. It is, therefore, desirable to consider the fourth-degree term as well. This is also considerably less than the fourth-degree term in Eq. (8) of I, but by no means negligible. In fact, the fourth-degree term is itself sufficient to cause a change of more than 40 percent in d^2E_p/da^2 over a range of a of 0.1A. It is, of course, true that the fourth-degree term can be determined only roughly. But, since greater displacements than 0.1A may be expected, even for the zero-point vibrations, there seems to be no reason to doubt that the reasons given in I for the breakdown of the previously derived[7] relation between Θ and E_p are substantially correct as there given.

Over the range of a from 3.82A to 3.86A, which about covers the expansion of the solid from 0°K to the melting point, the appearance of the E_p *vs.* a curve is not greatly changed from that given by Eq. (8) of I. (See Fig. 1 of I.)

Equation (7) above gives a value of $-E_p$ about 2.2 calories per mole lower at 3.82A, about 0.7 calories lower at 3.83A, about 0.8 higher at 3.84A, about 1.4 calories higher at 3.85A, and about 0.2 calories higher at 3.86A. Outside this range, where the E_p *vs.* a curves represent extrapolations, the differences are naturally greater. In particular, the minimum of E_p (and correspondingly the minimum of the interatomic potential curve) given by Eq. (7) is displaced by approximately 0.01A toward smaller values of a as compared to that given by Eq. (8) of I. However, these differences can hardly affect the qualitative relationship between the curves shown in Fig. 2 of I. It should be emphasized that the most important difference between the two curves shown in Fig. 2 of I is their difference in slope in the experimental range of a. It will be clear that this difference is scarcely altered by the present work. We, therefore, conclude here, as in I, that the slope of the E_p *vs.* a curve in the experimental range, obtained by direct application of the Debye theory to the experimental data, is much greater than that expected from the attempt[7] to derive a relation between E_p and Θ; and, as stated above, that the attempted derivation fails because of the extreme anharmonicity of the interatomic potential curve, which means that the theory of small vibrations cannot be applied.

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The Thermodynamic Properties of Liquid Argon

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The thermodynamic properties and equation-of-state data of liquid argon are interpreted in terms of a partition function previously derived. This partition function has a part due to vibratory motion of the atoms in the liquid and a part due to translational motion. The vibratory part contains the Debye characteristic temperature Θ for the solid, evaluated for a certain interatomic distance a_0 which appears as a parameter in the partition function. a_0 is interpreted as the average interatomic distance between nearest neighbors in the liquid, and is a function of a, the latter being defined as $(2^{\frac{1}{2}}V/N)^{\frac{1}{3}}$, where V is the molal volume and N Avogadro's number. With V set equal to the molal volume of the liquid at its normal melting point, a_0 is assigned a value which appears reasonable from the atomic distribution curves obtained by x-ray studies of the liquid. With this value of a_0, the partition function for this fixed value of V gives reasonably good values of the entropy over a large range of temperatures. A small, entirely reasonable change in the partition function improves the agreement with the experimental data. The parameters in the partition function have been evaluated for other values of V by using equation-of-state data. This leads to a calculation of the specific heats of saturated liquid argon over a range of temperatures. The agreement with experimental data is not exceedingly close, but is probably within experimental error. A calculation is also made of the free energies of the solid and liquid phases along the melting curve. They are found to be equal to within reasonably close limits. The application to various values of V leads to the evaluation of a_0 as a function of a. The experimental curve for $(\partial S/\partial V)_T$ plotted against V appears to show a change of slope near the value of V characteristic of the liquid at its normal melting point. There is also a change in slope of the curve for da_0/da *vs.* a, at the corresponding value of a. These facts are interpreted in terms of the atomic distribution curves, which appear to indicate a change in structure of the liquid which starts near the same value of V or a. The liquid appears to change from a distorted face-centered structure to a distorted body-centered structure as the volume increases. Information about the potential energy of liquid argon is obtained from the experimental data by application of the partition function. It is found that the potential energy of the liquid can be rather effectively correlated with the potential energy of the solid. Finally, certain peculiarities of the equation-of-state data are believed to indicate a prefreezing phenomenon, in which particles containing appreciable numbers of atoms and having the structure of the solid, appear in the liquid. A state of this sort can be stabilized by the entropy of mixing of the solid particles with the liquid.

1. THE GENERAL THEORETICAL EQUATIONS.

IN a paper entitled "On the Statistical Mechanics of Liquids, and the Gas of Hard Elastic Spheres" [1] (referred to hereafter as SML) I proposed the following partition function for

[1] O. K. Rice, J. Chem. Phys. **12**, 1 (1944).

the thermal part of the energy of a monatomic liquid in a not too expanded state, and at a temperature such that classical considerations apply:

$$Q=Q_0^3 =[(2e)^{\frac{1}{2}}T/\Theta+(2\pi mkT/h^2)^{\frac{1}{2}}2^{-1/6}e(a-a_0)]^3. \quad (1)$$

In this equation Q is for one atom; Q_0, which is introduced here for convenience, is for one degree of freedom. The symbols used have the following significance:

T = absolute temperature,
Θ = Debye characteristic temperature of the *solid*, evaluated for such a degree of compression of the solid that the distance between nearest neighbors is a_0,
m = mass of an atom,
k = Boltzmann's constant,
h = Planck's constant,
a = the distance between neighbors which would be found if the liquid were a close-packed cubic lattice having the same density.

We have

$$a^3=2^{\frac{1}{2}}V/N, \quad (2)$$

where V is the molal volume and N is Avogadro's number. The quantity a_0 is a parameter; a_0 is always less than a. For the present purposes it is to be considered as a function of a (though when a more exact theory becomes possible, it may be found better to take it as a variable parameter to be found by minimizing the free energy).

The interpretation of a_0 and the justification for the use of Eq. (1) are explained in SML. It there appears that if we had a gas or liquid of hard elastic spheres of radius σ we could write

$$Q_0=(2\pi mkT/h^2)^{\frac{1}{2}}2^{-\frac{1}{2}}e(a-\sigma). \quad (3)$$

In the case of the real liquid with a force field between the atoms, part of this quantity is replaced by the term $(2e)^{\frac{1}{2}}T/\Theta$. a_0 may, therefore, be described as a parameter which divides the space available to any degree of freedom into a part where the motion is translational and a part where it is vibrational. As pointed out in Section 4 of SML, we can consider two types of motion of atoms, one a long range motion in which the atoms move relatively great distances and exchange places, and one a short range motion. The first type is translational and the second type vibrational; any one degree of freedom, however, rapidly and frequently shifts from one type to the other. Both types of motion are possible even in the case of hard elastic spheres, though in this case the "vibrational" type of motion is actually force-free. The vibrational motion is the short range type, one atom between its neighbors, not involving the longer motions involved in exchanges of position. It, therefore, seems reasonable to identify a_0, at least in simple cases, and at least approximately, with the actual average distance between centers of molecules which can be described as nearest neighbors in the liquid. Thus we understand that Θ is to be considered as a function of a_0, and we may expect the potential energy of the liquid to depend on a_0. This, of course, is not an exact statement; it may, however, be expected to contain a considerable element of truth, and does in fact lead to interesting correlations of the properties of the liquid with those of the solid, as we shall see.

We shall find it convenient to rewrite Eq. (1) in the form

$$Q_0=LT/\Theta+MT^{\frac{1}{2}}(a-a_0), \quad (4)$$

where the meanings of L and M are defined by the equations. We can then concisely define certain useful quantities:

$$B=T(\partial Q_0/\partial T)_V=LT/\Theta+\tfrac{1}{2}MT^{\frac{1}{2}}(a-a_0), \quad (5a)$$

$$D=T(\partial B/\partial T)_V=LT/\Theta+\tfrac{1}{4}MT^{\frac{1}{2}}(a-a_0). \quad (5b)$$

Also we have

$$(\partial Q_0/\partial a)_T=-(LT/\Theta^2)(d\Theta/da_0)da_0/da +MT^{\frac{1}{2}}(1-da_0/da). \quad (6)$$

As noted above, the partition function takes into account only the thermal energy. The thermal energy, by the normal process of logarithmic differentiation of the partition function, is found to be, per mole (i.e., per $3N$ degrees of freedom),

$$E_t=3RTB/Q_0. \quad (7)$$

The molal work function, A, is given by

$$A=-3RT\ln Q_0+E_p, \quad (8)$$

where E_p is the potential energy per mole and is a function of a only. E_p is the energy the system would have if, without change of volume and without crystallization, it were reduced to absolute zero, and if there were no zero-point

TABLE I. Properties of liquid argon at its normal melting point.

Property	Source	Value
a	Baly and Donnan[a,b]	4.038A
a	Mathias et al.[c,d]	4.048A
a	Bridgman[e]	4.038A
a	Used in this paper[f]	4.037A
ΔV, fusion	Clusius and Weigand[g]	3.53 cc mole^{-1}
ΔV, fusion	Bridgman [c,e]	3.18 cc mole^{-1}
$\alpha[=V^{-1}(\partial V/\partial T)_P]$	Baly and Donnan[a,b]	0.0045 deg.$^{-1}$
α	Mathias et al.[c,d]	0.0042 deg.$^{-1}$
C_v	Eucken and Hauck[h,a]	5.5 cal. mole^{-1} deg.$^{-1}$
C_p	Eucken and Hauck[h,a]	10.5 cal. mole^{-1} deg.$^{-1}$
C_p	Clusius[a,i]	10.0 cal. mole^{-1} deg.$^{-1}$
$(\partial P/\partial T)_V$	Bridgman[e]	0.556 cal. deg.$^{-1}$ cc^{-1}
$(\partial P/\partial T)_V$	Simon and Kippert[j]	0.60 cal. deg.$^{-1}$ cc^{-1}
ΔS, fusion	Clusius and Weigand[g]	3.35 cal. mole^{-1} deg.$^{-1}$
ΔS, fusion	Bridgman[c,e]	3.12 cal. mole^{-1} deg.$^{-1}$

[a] Involves slight or quite certain extrapolation.
[b] See reference 8.
[c] Involves appreciable extrapolation.
[d] See reference 7.
[e] See reference 6.
[f] Consistent with V(calc.) of Table I of reference 9.
[g] See reference 11.
[h] A. Eucken and F. Hauck, Zeits. f. physik. Chemie **134**, 161 (1928).
[i] See reference 10.
[j] F. Simon and F. Kippert, Zeits. f. physik. Chemie **135**, 113 (1928).
For numbered references see citations in text.

energy. The zero-point energy does not need to be considered at all, in our case, since we deal only with temperatures sufficiently high so that the system may be thought of as classical. The energy E_t does actually include some potential energy in virtue of the vibrations of the atoms about their positions of equilibrium in the field of their neighbors. E_p might perhaps be more exactly defined as the lowest possible potential energy for the liquid at the molal volume V.

The various thermodynamic quantities can now be obtained in terms of the quantities already defined. We have for the molal entropy,

$$S=-(\partial A/\partial T)_V=3R\ln Q_0+3RB/Q_0, \quad (9)$$

and for the pressure

$$P=-(\partial A/\partial V)_T =(3RT/Q_0)(\partial Q_0/\partial V)_T-dE_p/dV. \quad (10)$$

Also

$$(\partial S/\partial V)_T=(\partial P/\partial T)_V =(3R/Q_0)[(\partial Q_0/\partial V)_T+(\partial B/\partial V)_T -(B/Q_0)(\partial Q_0/\partial V)_T], \quad (11)$$

and for the specific heat at constant volume

$$C_v=3R[(B/Q_0)+(D/Q_0)-(B^2/Q_0^2)]. \quad (12)$$

Derivatives with respect to V may be replaced by derivatives with respect to a by means of Eq. (2), and Eq. (6) and a similar equation for $(\partial B/\partial a)_T$ may be used to get explicit expressions. For future reference we write down the expression for P:

$$P=\frac{2^{\frac{1}{2}}RT}{a^2NQ_0}\left[-\frac{LT}{\Theta^2}\frac{d\Theta}{da_0}\frac{da_0}{da}+MT^{\frac{1}{2}}\left(1-\frac{da_0}{da}\right)\right] -\frac{2^{\frac{1}{2}}}{3a^2N}\frac{dE_p}{da}. \quad (13)$$

It is now proposed to use the equations just developed as a guide in the study of the properties of liquid[2] argon. In doing this we shall adhere to the philosophy followed in a number of earlier papers[3] in which the approach was frankly semi-empirical. The equations do not suffice in themselves for a complete description of the liquid without reference to the experimental data, since we do not have sufficient information concerning some of the quantities involved in them. In particular, we do not know a_0 as a function of a, since we do not have a sufficiently detailed knowledge of the complicated geometry of a more or less random distribution of atoms. It does appear, nevertheless, that the equations offer a reasonably good guide for the handling of the experimental data, and for finding relations which might not otherwise be discovered.

It may be well to note that our method of handling the parameter a_0 is somewhat different from the procedure

[2] We use the term liquid to describe the amorphous phase if its density is greater than the critical density, regardless of the temperature. This is a consistent usage from our point of view since the properties are continuous at the critical temperature.
[3] O. K. Rice, J. Chem. Phys. **7**, 136, 883 (1939).

used in the earlier work.[3] In this earlier study, instead of a_0, we used the concept of the average coordination number of the atoms in the liquid. This quantity was treated as though it were an extra variable of state, determined under any fixed set of conditions by the fact that the free energy of the system had to be a minimum. An attempt[3,4] was made to estimate the effect of this variable on the energy and entropy of the system, in order that the result of minimizing the free energy might be determined, and these attempts have been continued since. However, they were not entirely successful, and it became evident that the geometry of the system was too complicated to permit this program to be carried to completion. The later work indicated[5] that the approach outlined above might be more practicable and successful.

2. EXPERIMENTAL PROPERTIES OF ARGON

It is convenient to start with a summary of the properties of argon at its normal melting point, 83.78°K, and atmospheric pressure; this is given in Table I where sources are indicated.

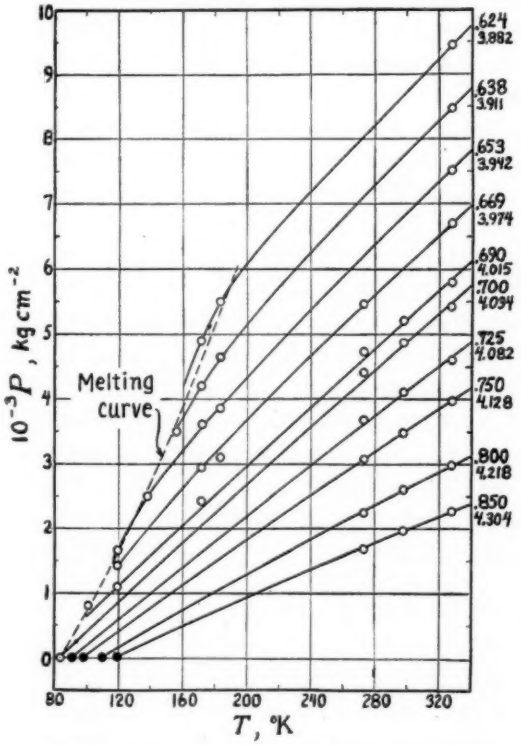

FIG. 1. Equation-of-state data for argon. The curves connect points for constant volume; the number at the right-hand end of each curve gives the volume in cc/g. The number just below the volume gives the value of a. Open circles are from Bridgman; black circles are from Mathias, Onnes, and Crommelin. The relation between the melting curve and the constant-volume curves is such as to indicate somewhat different values of the volume of the liquid along the melting curve than those given by Bridgman. At 2000, 4000, and 6000 kg/cm² we find, respectively, 0.654, 0.633, and 0.622 cc/g.

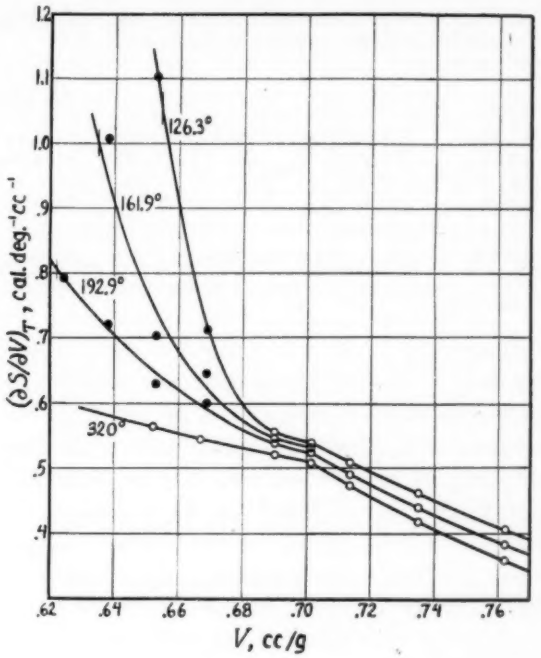

FIG. 2. $(\partial S/\partial V)_T$ curves. The open circles are taken or interpolated directly from Table V (this table was also used to assist in construction of the curves of Fig. 1, as noted in text). The black circles are taken from measurements of slopes of curves in Fig. 1. Each circle in every case belongs to the curve nearest it.

The other data which are available consist principally of equation-of-state data due to Bridgman[6] and to Mathias, Onnes, and Crommelin.[7] These are summarized in Fig. 1. The open circles are interpolated (in some cases there are slight extrapolations) from Bridgman's data, and give the variation of pressure with temperature for a number of constant volumes, as indicated. The points for a given volume are connected by curves, whose shapes are in part determined by theoretical considerations, as will be described below. The black circles are from Mathias, Onnes, and Crommelin's data. Their volumes have been corrected slightly so that they will be consistent with the specific volumes of Baly and Donnan[8] and of Bridgman, which agree well with each other (see note to Table V, below).

[4] O. K. Rice, J. Chem. Phys. **10**, 654 (1942) (in this note the "number of holes" was used as a variable instead of the coordination number).

[5] See reference 1, page 17.

[6] P. W. Bridgman, Proc. Am. Acad. **70**, 1 (1935).

[7] E. Mathias, H. K. Onnes, and C. A. Crommelin, Proc. Roy. Acad. Sci. Amsterdam, **15**, 667, 960 (1912); C. A. Crommelin, *ibid.* **13**, 54 (1910); **16**, 477 (1913).

[8] E. C. C. Baly and F. G. Donnan, J. Chem. Soc. London **81**, 907 (1902).

TABLE II. Entropies of solid and liquid argon at various temperatures in calories per mole per degree.

T(°K)	S_{solid}	ΔS_{fus}	ΔS_{expan}	S_{liquid} ($a=4.037$)
83.78	9.07*	3.35	0.00	12.42
126.3	11.39	2.07	1.28	14.74
161.9	12.65	1.59	1.78	16.02
192.9	13.43	1.34	2.01	16.78

* Though calculated from the same data, this is 0.05 lower than the value given by K. Clusius and A. Frank, Zeits. f. Elektrochemie **49**, 308 (1943), which has recently come to my attention; the difference is not important.

Figure 2 gives the value of $(\partial P/\partial T)_V$ or $(\partial S/\partial V)_T$, converted to cal. cc^{-1} deg.$^{-1}$, for several selected temperatures, as obtained from the curves of Fig. 1. Figure 2 will be discussed in detail in a later section, but will be found useful here in enabling us to determine the entropy of the liquid at its normal volume, where $a=4.037$, at various temperatures. For this purpose it is necessary to find first the entropy of the solid in equilibrium with the liquid at various temperatures. This is obtained from the values of Θ found for $\Gamma=0.18$ in Table I of the preceding article.[9] We then obtain the change of entropy on fusion (ΔS_{fus}) from the heat of fusion as given by Clusius[10,11] at the normal melting point of 83.78°K and by Bridgman at the higher temperatures. Finally, for the higher temperatures, we obtain the entropy of expansion (ΔS_{expan}) of the liquid from its volume when in equilibrium with the solid to its "normal" volume, for which $a=4.037$, by integrating the $(\partial S/\partial V)_T$ values. The limits of integration are shown on the curves in Fig. 2 by short vertical lines. For consistency these volumes are adjusted to conform to the calculated V's for the solid given for $\Gamma=0.18$ in Table I of the preceding article, using Bridgman's values of ΔV of fusion. The results are given in Table II.

3. APPLICATION OF THE EQUATIONS TO ARGON AT ITS "NORMAL" VOLUME

In attempting to apply the equations, we come at once to a difficulty, since, as noted above, we do not have any theoretical way to find a_0 as a function of a. However, the considerations of Section 1 do indicate that a_0 may be approximated by the average distance between nearest neighbors. The atomic distribution in argon has been studied by Lark-Horovitz and Miller[12] and by Eisenstein and Gingrich,[13] who agree that near the freezing point the first maximum in the distribution curve of liquid argon occurs at 3.79 or 3.80A, within about 1 percent. The average distance of nearest neighbors is slightly displaced toward greater distances, though it is not too exactly defined because of the broadness of the maximum. We have, therefore, carried out computations of a number of the thermodynamic quantities for $a=4.037$A and $a_0=3.82$A, 3.85A, and 3.88A. These are given in Table III. In this table S and C_v are calculated directly from Eq. (9) and Eq. (12) from the value of a_0 given, determining Θ from a_0 by use of the preceding article. L and M are evaluated as indicated by comparison of Eqs. (4) and (1) using Birge's values of the constants.[14] We have evaluated da_0/da and dE_p/da empirically by using two experimental values of the pressure (given in

TABLE III. Calculated thermodynamic properties of liquid argon at $a=4.037$A, $L=1.7584$, $M=0.8769A^{-1}$ deg.$^{-1}$.

a_0	3.82			3.85				3.88		
da_0/da	0.487			0.441				0.411		
dE_p/da	993			1067				1128		
T	83.78	192.9	320	83.78	126.3	192.9	320	83.78	192.9	320
S	12.08	16.27	18.92	12.19	14.29	16.51	19.23	12.35	16.80	19.59
C_v	4.88	5.17	5.31	5.05	5.19	5.31	5.43	5.23	5.45	5.54
P	(0)	58.1	(123.9)	(0)	23.3	58.7	(123.9)	(0)	59.2	(123.9)
$(\partial S/\partial V)_T$	0.544	0.524	0.514	0.562	0.540	0.523	0.505	0.571	0.523	0.499

Units: a_0 and a in A; E_p in cal. mole^{-1}; T in °K; S and C_v in cal. mole^{-1} deg.$^{-1}$; P in cal. cm^{-3}; V in cm^3 mole^{-1}. To convert P to kg/cm^2 divide by 0.02343.

[9] O. K. Rice, J. Chem. Phys. **14**, 321 (1946).
[10] K. Clusius, Zeits. f. physik. Chemie **B31**, 459 (1936).
[11] K. Clusius and K. Weigand, Zeits. f. physik. Chemie **B46**, 1 (1940).
[12] K. Lark-Horovitz and E. P. Miller, Nature **146**, 459 (1940).
[13] A. Eisenstein and N. S. Gingrich, Phys. Rev. **62**, 261 (1942).
[14] R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).

TABLE IV. Calculated thermodynamic properties of liquid argon at $a=4.037$A, $L=1.9$, $M=0.8769$A^{-1} deg.$^{-1}$.

a_0	3.82			3.85				3.88		
da_0/da	0.494			0.453				0.425		
dE_p/da	984			1050				1109		
T	83.78	192.9	320	83.78	126.3	192.9	320	83.78	192.9	320
S	12.38	16.61	19.29	12.51	14.63	16.87	19.61	12.70	17.19	19.99
A				(0)	−580.0	−1634.2				
C_v	4.93	5.20	5.35	5.10	5.24	5.35	5.47	5.28	5.47	5.58
P	(0)	58.0	(123.9)	(0)	23.3	58.6	(123.9)	(0)	58.9	(123.9)
$(\partial S/\partial V)_T$	0.542	0.526	0.514	0.556	0.538	0.524	0.507	0.565	0.522	0.502

Units: A in cal. mole^{-1}; for the others see Table III.

parentheses) in Eq. (13), thus setting up two simultaneous equations of the form of Eq. (13). Since Θ and $d\Theta/da_0$ are known from the preceding article, and all other quantities are also known except da_0/da and dE_p/da (which are the same in the two simultaneous equations, since they depend only on a, not on T), we can solve for the latter two quantities. Having done this, the values of P not enclosed in parentheses are obtained from Eq. (13), and the values of $(\partial S/\partial V)_T$ from Eq. (11).

It will be observed that none of the thermodynamic quantities depend strongly on the value chosen for a_0. However, the values of S are a little low as compared to those given in Table II. Since S does show a slight increase with a_0, this discrepancy could be lessened by going to larger values of a_0, but it is felt that a value of a_0 too much larger than that for the maximum in the atomic distribution curve should not be used.

On page 16 of SML the value of L was determined by certain considerations concerning the relaxation of the effect of "side-atoms" on going from the solid to the liquid state. If we imagine an atom vibrating in a crystal lattice directly toward one nearest neighbor and directly away from the opposite one, the field of force in which it moves is also influenced by the atoms off at an angle, these being fixed in their positions in a lattice. This means that Θ for the solid is roughly $2^{\frac{1}{2}}$ times as great[15] as it would be if these side-atoms did not exist. In the liquid it is assumed that these side-atoms, not being fixed in position, but being free to move, on the average adjust themselves about an atom which happens to be displaced toward one of its neighbors and away from the opposite one. Thus, since we use Θ for the solid in our partition function, we should divide Θ by $2^{\frac{1}{2}}$. Actually, however, the side-atoms do have space-filling properties, which reduces the free space available to the vibrating atoms, and the net result is that Θ should be divided by $2^{\frac{1}{2}}/2^{\frac{1}{3}}$ or $2^{\frac{1}{6}}$. Now since there are fewer nearest neighbors in the liquid than in the cubic close-packed solid argon, the space-filling properties of the neighbors may not be quite so great as for the solid; furthermore, if an atom in a liquid is displaced toward one neighbor, there will not in general be another neighbor *exactly* opposite. This suggests that there may be a little greater relaxation in the liquid than is given by dividing Θ by $2^{\frac{1}{6}}$, and that, therefore, we should take a slightly larger value for L than that given[16] in Table III. We have, therefore, tried $L=1.9$, and have obtained the results shown in Table IV. To this table we have, for reasons which will appear later, added, in one case, values of the molal work function A, taken arbitrarily zero at the normal melting point.

It is seen that with $a_0=3.85$ we have achieved quite satisfactory agreement with the entropy values given in Table II. It may, of course, be

[15] Exactly, if only nearest neighbors are effective, and the lattice is cubic close-packed.

[16] The considerations of SML dealing with the gas of hard elastic spheres (before the effect of interatomic forces was taken into account at all) indicate the possibility that the partition function in Eq. (3) above may be an underestimate from another cause (see p. 13, especially Fig. 5, of SML). This would mean that Q_0 in Eq. (1) would also be an underestimate. This would cause an increase in the whole expression in brackets in Eq. (1), rather than just in the first term, but would have about the same effect. On the other hand, the communal entropy was handled in such a way as to make the equations give an overestimate for Q_0 (see Section 1 of SML), so these effects counterbalance each other to a greater or less degree. It may be remarked, however, that the relaxation of the effect of the side-atoms could possibly cause some increase in the communal entropy carried by the vibrational term in Q_0 over that characteristic of a Debye solid, especially since in the latter the communal entropy is not fully excited (see page 7 of SLM).

TABLE V. Calculated thermodynamic properties of argon at various volumes, $L=1.9$, $M=0.8769$.

a	4.15	4.10	4.06	4.037	4.015	3.97	3.94
a_0	3.8912	3.8753	3.8600	3.85	3.8400	3.8195	3.8058
da_0/da	0.287	0.351	0.415	0.453	0.456	0.456	0.456
dE_p/da	1057	1070	1065	1050	962	740	547
T_{sat}*	101.58	94.24	87.75	83.78	100		
P at T_{sat}	(0.1)	(0.0)	(0.0)	(0.0)	15.1		
P at 192.9°	36.5	44.9	53.2	58.6	66.2		
P at 320°	(83.6)	(99.3)	(114.4)	(123.9)	(133.2)	(155.4)	(173.8)
$(\partial P/\partial T)_V$ at T_{sat}	0.416	0.474	0.525	0.556	0.565		
$(\partial P/\partial T)_V$ at 192.9°	0.384	0.440	0.489	0.524	0.538		
$(\partial P/\partial T)_V$ at 320°	0.361	0.419	0.473	0.507	0.520	0.544	0.563
$(10.5/12)(da_0/da)(dE_{p,s}/da_0)$†	536	610	645	639	565	360	190

* T_{sat} is the temperature at which the liquid having the given value of a is in equilibrium with its vapor (except for $a=4.015$, where the lower temperature was taken arbitrarily). These temperatures were obtained from the data of Mathias, Onnes, and Crommelin (see reference 7), their values being slightly corrected so as to conform to Baly and Donnan's value (see reference 8) at the melting point, but so as to be consistent with their own values of α, as given in Table VI.

† See Section 7, subsection, "Potential Energy of Liquid Argon."

said that this is obtained only by the use of two adjustable constants, a_0 and L. However, the adjustment of L is really quite small, it being increased over the originally estimated value by only 8 percent, while the value of a_0 used is entirely reasonable, and the results are not extremely sensitive to it. In any event, we have matched three values of S reasonably well with the value of a_0 used, and the only slightly adjusted value of L. Furthermore, the curve for P against T comes out to be almost a straight line, which is obviously correct as indicated in Fig. 1, though too much stress on this point must not be laid, since presumably any reasonably sensible theory would give this result.

TABLE VI. Specific heats of saturated liquid (calories per mole per degree).

T(°K)	83.78	87.75	94.24	101.58
a(A)	4.037	4.06	4.10	4.15
α(deg.$^{-1}$)$\times 10^3$*	4.20	4.38	4.74	5.23
C_v(obs.)**		5.50	5.50	5.50
C_p(obs.)**		10.5	10.72	11.04
C_p(obs.)†		10.06		
C_v(calc.)	5.10	5.10	5.08	5.04
C_p-C_v(calc.)	5.49	5.75	6.20	6.73
C_p(calc.)	10.59	10.85	11.28	11.77

* Mathias, Onnes, and Crommelin, reference 7 (values at 83.8 and 87.75 obtained by extrapolation).

** Eucken and Hauck, reference h, Table I. (Actually the specific heat at saturation was measured, but over the range involved this is essentially C_p.)

† Clusius, reference 10.

TABLE VII. Entropies and specific heats at $a=4.037$A (calories per mole per degree).

T(°K)	83.78	126.3	161.9	192.9
S (Table II)	12.42	14.74	16.02	16.78
S (Table IV)	12.51	14.63	15.94	16.87
$C_{v,Av.}$ (Table II)	5.63	5.1	4.3	
$C_{v,Av.}$ (Table IV)	5.17	5.3	5.3	

We shall return to a discussion of the specific heat values in Section 5.

4. APPLICATION OF THE EQUATIONS TO ARGON AT VARIOUS VOLUMES

By combining the results of Bridgman and Mathias, Onnes, and Crommelin, as presented in Fig. 1, we have a series of data at high temperatures and at one much lower temperature for each of a number of volumes greater than the "normal" volume of melting argon; i.e., values of a greater than 4.037A. These data can be used in the same way as the data at $a=4.037$A to obtain values of da_0/da and dE_p/da, as well as the various thermodynamic quantities. Starting with $a_0=3.85$A at $a=4.037$A, a_0 at any other value of a will be determined by integration of da_0/da; on the other hand, da_0/da at any given a itself depends upon the corresponding value of a_0. It is, therefore, obvious that it is necessary to make successive adjustments to assure consistency in this matter. This, however, is relatively easy, because the dependence of da_0/da on a_0 at a given a is slight.

For values of a less than 4.015, we see from Fig. 1 that the slopes of the P *vs.* T curves change sharply at the lower temperatures. On the basis of Eq. (13) this is a distinctly "abnormal" behavior. This "abnormal" behavior will be discussed later; we believe that the high temperature ends of these curves are "normal." Unfortunately, there is in each of these cases only one experimental point at a high temperature, so the slope in this region can only be inferred. The curves for $a \leq 4.015$ shown in Fig. 1 are drawn

with slopes (for the high temperature ends of the curves) calculated from Eq. (11) on the assumption that as a goes below 4.037 the value of da_0/da reaches a limit of 0.456. It is obvious that the slopes shown in Fig. 1 cannot be greatly in error, but some more experimental work in this region would be most welcome.

The calculations mentioned in the above two paragraphs are summarized in Table V. Again pressures which are obtained directly or by interpolation from the experimental data are given in parentheses. It was these which were used for $a \geq 4.037$ to calculate da_0/da and dE_p/da. (For $a=4.015$ it was assumed, as noted above, that $da_0/da=0.456$ and P at 100° was then calculated). In all cases the values of Θ necessary for the calculations were obtained from a_0, using Eqs. (1) and (2) of the preceding article, taking $\Gamma=0.18$.

The curves given in Fig. 1 were all drawn with the aid of the values of P and $(\partial P/\partial T)_V$ given in Table V (except for the low temperature ends of those with $a<4.015$). Since the values of a in Table V and Fig. 1 do not all coincide, interpolation, or, in some cases, extrapolation, was necessary in order to construct the curves.

5. THE SPECIFIC HEATS

The data on the specific heat of the liquid are summarized in Tables VI and VII. The data in Table VI refer to liquid in equilibrium with its vapor. C_v(calc.) comes directly from Eqs. (5) and (12) using Table V. C_p-C_v(calc.) is obtained from the formula

$$C_p-C_v=\alpha VT(\partial P/\partial T)_V, \qquad (14)$$

α is obtained from the density measurements of Mathias, Onnes, and Crommelin[7] (these all being made at what amounts essentially to zero pressure). $(\partial P/\partial T)_V=(\partial S/\partial V)_T$ is taken from Table V, or, what is the same thing, from Fig. 1.

In Table VII the average C_v's were calculated from the changes in entropy with temperature; the values from Table II are essentially the "experimental" values, though some calculation is involved in them, also, since they depend on the entropy of the solid, which has not been measured directly. To the values of Table IV one at 161.9° has been added.

It will be seen from Table VI that our calculated values of C_v are somewhat lower than the experimental values of Eucken and Hauck. This discrepancy seems to be confirmed by Table VII in view of the difference between the experimental and calculated C_v's for the range between 83.78° and 126.3°. On the other hand if the calculated value of C_v at 83.8°, given in Table VI, is too small, then the calculated C_p-C_v must be too large; otherwise, C_p would considerably exceed the experimental value. However, C_p-C_v is actually pretty well tied to the experiments. The value of $(\partial P/\partial T)_V$ used in Eq. (14), from which C_p-C_v is calculated, is one which fits Bridgman's data as shown in Fig. 1; in fact, the only role of the theory here is to indicate the variation of $(\partial P/\partial T)_V$ with the temperature. The data do not definitely exclude a slightly different curvature of the P *vs.* T curve. $(\partial P/\partial T)_V$ might have a lower value than that given in Table V, at the lower end of the curve, and a higher value at the upper end; the theory may be wrong in this respect, though it seems unlikely.[17] Furthermore, the independent direct measurement by Simon and Kippert of $(\partial P/\partial T)_V$ for the normal liquid gives a value *greater* than that inferred from Bridgman's data (see Table I). Also, in applying Eq. (14) we have used the smaller of the two values of α, a value which was in fact obtained by extrapolation. In other words, our estimate of C_p-C_v appears to be about the least possible. It, therefore, seems justifiable to say that there are inconsistencies between various sets of experimental data as great as any errors in the theory. We may note further that, while we have no direct check on the C_v values of Eucken and Hauck, disagreements appear in other thermal measurements. Thus the C_p values of these authors do not agree exactly with

[17] A slight decrease in $(\partial P/\partial T)_V$, that is $(\partial S/\partial V)_T$, with increasing temperature seems normal from general considerations. In contrast to a liquid composed of hard elastic spheres, which would, at any given total volume, have a free volume independent of temperature, the free volume of a real liquid increases with temperature. Hence a given increase in total volume should have a smaller *relative* effect on the free volume at a higher temperature, so that $(\partial S/\partial V)_T$ should be smaller.

We may look at this matter in another way. We have

$$[\partial(\partial S/\partial V)_T/\partial T]_V=[\partial(\partial S/\partial T)_V/\partial V]_T=T^{-1}(\partial C_v/\partial V)_T.$$

But as the liquid expands and becomes more gas-like, C_v should decrease, and $(\partial C_v/\partial V)_T$ should be negative, which means, then, that $(\partial S/\partial V)_T$ decreases with increasing temperature.

Clusius. Clusius has noted that his C_p's for solid argon are 1 to 6 percent lower than earlier values of Eucken, while his value of the heat of fusion is considerably higher than that of Eucken.

Turning to Table VII, we see that the calculated trend of C_v values is upward with increasing temperature, while the experimental values appear to decrease. Here, again, the theory reflects the normal expectation. A slight rise of C_v with temperature is to be expected because the vibratory motion, as compared to the translational, should become relatively more prominent at the higher temperatures where its amplitude increases.

We note that if the entropies at 126.3° and 161.9° from Table II were lower by about 0.2 entropy units, the discrepancy in the C_v values would be removed. An error of this magnitude is perhaps not beyond the limits of experimental inaccuracy, since it would be only 6 percent of the entropy change of about 3.35 units which occurs in going from melting solid to liquid with $a=4.037$A.

Since the relation $(\partial S/\partial V)_T=(\partial P/\partial T)_V$ holds, whether the system is undergoing a change of phase or not, the discrepancy would be removed if Bridgman's dP/dT for the melting curve, and the average ordinates of the curves for 126.3° and 161.9° in Fig. 2 above, were all too high by 6 percent. The curves of Fig. 2 certainly may well be in error by this amount. And there is some suggestion from the more recent though less extended melting curve of Clusius and Weigand[11] that Bridgman's melting curve may be this much in error. At 0° and the normal melting point, Clusius and Weigand found $dP/dT=40.5$ kg/cm^{-2} deg.$^{-1}$, while Bridgman's value is 42.0. (The discrepancy is not so great as indicated by Clusius and Weigand, who must have made an incorrect conversion of units.) However, the curvature of Clusius and Weigand's P *vs.* T curve is very much greater than that of Bridgman's, so that already at about $P=200$ kg/cm^2, the limit of Clusius and Weigand's pressure range, the two slopes become equal. Assuming the careful measurements of Clusius and Weigand to be correct over their limited range of pressures, the question arises as to whether, with rising pressure, the slope is correctly given by Bridgman's data, or whether it continues to increase. If the latter occurs, the true pressures, which (assuming them to be given by Clusius and Weigand's data) at temperatures very close to the normal melting point lie below Bridgman's curve, would soon cross it. If the true pressures again crossed Bridgman's curve around 135°K, there would be a region where the slope was a little less than that given by Bridgman. This could happen without any of Bridgman's temperatures being in error by more than about ±1 to 1.5°, but there would be a slight inflection in the P *vs.* T curve. Such an inflection would not be surprising if it were associated with the prefreezing phenomenon mentioned later in the paper. However, as noted in Section 6, there is a small discrepancy between the free energies of the liquid and solid along the melting curve, which would be somewhat increased if new experiments should confirm changes such as are suggested. Furthermore, it is difficult to make a complete analysis of the situation because of the way various experimental errors may interact with each other.[18] So the above analysis is not to be taken too literally, but it does suggest that the calculated values in Table VII are correct to within experimental error. Complete consistency between all possible data analyzed on the basis of our theory, is perhaps too much to hope for, in view of our rather bold use of the Debye theory of the solid, when there are strong indications[19] that it may need some modification on account of anharmonicities in the vibrations of the atoms.

The calculated value of C_p-C_v, as presented in Table VI, rises much more rapidly with temperature than the experimental values of Eucken and Hauck. We again recall that the calculated value of C_p-C_v is closely tied to experimental data, but it is again true that the data of Fig. 1 do not exclude somewhat smaller values of $(\partial P/\partial T)_V$ at the lower end of the curves. Any change in curvature of the P *vs.* T curves sufficient to make $(\partial P/\partial T)_V$ increase with increasing temperature has the same objections as those previously noted.[17] Even if we assume that $(\partial P/\partial T)_V$ is independent of temperature at $a=4.15$, say, C_p(calc.) for 101.58° is reduced only to 11.20 cal. mole^{-1} deg.$^{-1}$, and this value is based on the calculated C_v of 5.04, which is much lower than Eucken and Hauck's experimental value. I believe, however, that while the decrease in $(\partial P/\partial T)_V$ may not be as great as given in Table V, $(\partial P/\partial T)_V$ certainly will decrease with temperature to some extent. This, therefore, is further indication of error in some, at least, of the experimental results. The work of three sets of investigators enters into the comparison of values of C_p in Table VI, namely, that of Bridgman, that of Mathias, Onnes, and Crommelin, and that of Eucken and Hauck. While it seems unlikely that any one of these

[18] An error in the melting curve would not itself be without other complicating effects. A change would have to be made in the calculations of Table I of the preceding paper. These changes would be rather small, and the effect on the estimated entropy of the liquid (aside from that caused directly by changes in the slopes of the curves) could be neglected; but other changes in the experimental results might well result in unforeseen complications.

[19] O. K. Rice, J. Chem. Phys. **12**, 289 (1944); and see the preceding paper (reference 9).

pieces of work is sufficiently in error to account for the discrepancies involved, it may well be that the combined errors in all of them are great enough.

That this is a possibility is also suggested by some experiments on the velocity of sound in liquid argon made by Liepmann.[20] A slight extrapolation of his results gives a velocity of 8.30×10^4 cm/sec. at 87.75°K. The velocity of sound is given in terms of thermodynamic quantities by $(C_p-C_v)^{\frac{1}{2}}(C_p/C_v\alpha^2T)^{\frac{1}{2}}$ (see Liepmann's Eq. (5)). Using the values of α from Table VI and our calculated values of the specific heats (converted to ergs per gram) we obtain 8.73×10^4 cm/sec., about 5 percent too high. If we use, instead, the specific heats of Eucken and Hauck, the velocity is calculated at 7.73×10^4 cm/sec., about 7 percent too low.

In whatever way the questions raised in this section are ultimately settled, they do indicate one thing which is most important for the present; namely, there is a great need of new, highly accurate experimental work both on the thermal properties and the equation of state. The data now at hand represent excellent and beautiful pioneer work; but it is pioneer work and does not give a sufficiently detailed account of liquid argon to furnish a satisfactory basis for the theory. New measurements, using the best modern techniques, are urgently required.

In the meantime, since the theory seems to represent the various sets of experimental results within approximately the limits indicated by their mutual inconsistencies, it seems worth while to use it to make some calculations and deductions.

TABLE VIII. Free energy changes along the melting curve (calories per mole.)

T(°K)	$\Delta A_{t,s}$	P_mV_s	ΔE_p	ΔF_s	$\Delta A_{V,l}$	P_VV	I	ΔF_l
126.3	−432	1145	−5	708	−580	652	639	711
192.9	−1190	3374	−40	2144	−1634	1642	2145	2153

[20] H. W. Liepmann, Helv. Phys. Acta **12**, 421 (1939). Liepmann has noted the inconsistencies between his values and the thermal data. The inconsistency between his results and Eucken and Hauck's specific heat data would not appear to be quite so great had he used the values of α given in Table VI instead of the values given by Donnan and Baly; however they would still exist. It seems to me unlikely that the possible explanation offered by Liepmann, namely, that the sound wave is too fast to allow internal equilibrium to be established in the liquid, can be correct, since $\Theta=80$ corresponds to a frequency of about 1.7×10^{12}, far higher than the frequency of the sound wave used by him.

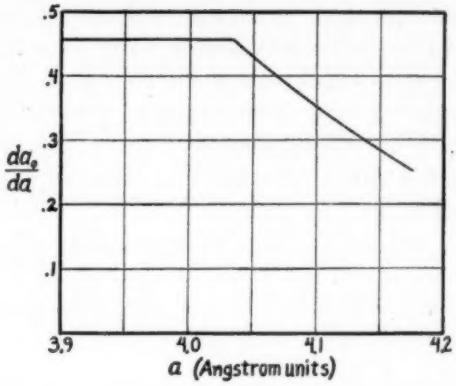

FIG. 3.

6. THE FREE ENERGY ALONG THE MELTING CURVE

Let us write ΔF_s for the free energy of the solid at any temperature and pressure, minus its free energy at zero pressure and its normal melting point at zero pressure; and let us write ΔF_l for the similar quantity for the liquid. Then at any point along the melting curve we should have

$$\Delta F_s=\Delta F_l. \tag{15}$$

We write

$$\Delta F_s=\Delta A_{t,s}+P_mV_s+\Delta E_p. \tag{16}$$

Here $\Delta A_{t,s}$ is the change in $A_{t,s}$, the thermal part of the work function of the solid, along the melting curve; it is readily computed, using the Debye theory, from the Θ's given in the preceding paper. P_m is the pressure along the melting curve, at the temperature of interest, and is known from Bridgman's work. V_s is the volume of the solid at the same temperature obtained from the V(calc.) of Table I of the preceding paper. The change in potential energy ΔE_p can be readily calculated, since E_p is known as a function of Θ from Eqs. (7), (1), and (2) of the preceding paper. As always, we use $\Gamma=0.18$.

For ΔF_l we write

$$\Delta F_l=\Delta A_{V,l}+P_VV+\int_{P_V}^{P_m}VdP. \tag{17}$$

Here $\Delta A_{V,l}$ is the change in work function at constant volume ($a=4.037$) (the A of Table IV). P_V is the pressure reached at the temperature of

interest at the constant volume V (with $a=4.037$); the values given in Table IV are used. The integral takes care of the change in F when the liquid is now compressed at constant temperature until solid begins to form, and can be evaluated from Bridgman's equation-of-state data (Fig. 1).

ΔF_s and ΔF_l and the other quantities in Eqs. (16) and (17) are given in Table VIII. The integral in ΔF_l is designated as I. Equation (15) is reasonably well satisfied.

We have noted that $\Delta A_{V,t}$ is calculated from the theoretical results of Table IV. Since some of the entropies in this table are higher than the experimental values and some lower, the average which goes into the equation $(\partial A/\partial T)_V=-S$ is about the same as if the experimental values had been used. However, if the experimental values in the middle temperature range were adjusted downward, as proposed in the preceding section, the discrepancy in Table VIII would be increased by use of the experimental values. This suggests that possibly the value of S at the normal melting point should be adjusted upward. This would have to represent a change in the ΔS of fusion, because if the entropy of the solid were also changed no net effect would result on the difference between ΔF_s and ΔF_l, since solid and liquid would be affected similarly. It seems unlikely, however, that there is any appreciable error in Clusius' value of the heat of fusion, so the normal ΔS of fusion should be well known. Although the difference between ΔF_l and ΔF_s is small, it seems more difficult to account for the discrepancy as experimental error than it does to account for the discrepancies involving the specific heats discussed in Section 5. The difficulty may be connected with the possible breakdown of the Debye theory of the solid, discussed in previous work,[19] and mentioned in Section 5. At the same time, it may be emphasized again that a complete reworking of the data on argon would be of the utmost value.

7. DISCUSSION

Behavior of da_0/da

In Fig. 3, we have plotted da_0/da against a. It will be noticed that there is a sharp break in the slope of this curve between $a=4.03$A and $a=4.04$A. This break corresponds to the break in $(\partial S/\partial V)_T$ for 320°K, coming at the same place as shown in Fig. 2. Though we cannot exclude the possibility that this break in the slope of the curves should be rounded off somewhat, there seems to be no doubt that the break in $(\partial S/\partial V)_T$ is real in the sense that there is a fairly marked change of slope in the region shown; the interpretation of it in terms of da_0/da depends upon our acceptance of the behavior of Θ with a_0 described in the preceding article.[21]

It might be possible to suppose that the break in the slope of the $(\partial S/\partial V)_T$ curve results from a change in the nature of the dependence of $d\Theta/da_0$, rather than of da_0/da on a_0. Especially might we consider this to be a possibility if the parameters were chosen (as is not excluded) in such a way that the value of a_0 involved was outside the experimental range of lattice distances in the solid where we have direct knowledge of the behavior of Θ. This would mean that we refer the break in slope of $(\partial S/\partial V)_T$ to a property of the solid rather than to a special property of the liquid. Aside from the inherent improbability of such an assumption, I believe that we can find some circumstantial evidence that the break is a distinct property of the liquid.

This rests on an examination[22] of the atomic distribution curves found by Eisenstein and Gingrich,[13] and by Lark-Horovitz and Miller.[12] Eisenstein and Gingrich found curves for liquid argon at 84.35°K and 91.8°K which differed very noticeably from each other. Each of these curves showed a maximum just below 3.8A, but there were 10.2 to 10.9 atoms under the first peak at 84.35°K and only 6.8 to 7.2 at 91.8°K, and the maximum was much lower in the latter case. Furthermore, at 91.8° there was a second peak at 4.7A, but at 84.35° there was a rather sharp minimum near this distance. Lark-Horovitz and Miller found a distribution curve at 89.2°K which appeared to be much more like the distribution curve at 84.35°K than that at 91.8°,

[21] The calculations of the earlier article (see reference 19), which the preceding paper modifies, led to a very radical variation of $d\Theta/da_0$ with a_0. Applied to the liquid, this made da_0/da increase rapidly with a, so that da_0/da became greater than 1 when the liquid was expanded somewhat beyond $a=4.037$A. This seemed very unreasonable because it meant that the compressibility of the individual atoms was greater than that of the liquid as a whole. At large values of a, we may, in fact, expect a_0 to approach a constant value, determined by the "size" of a single atom; da/da_0, then, should decrease asymptotically to zero. It was these considerations which led us to make the recalculation for the solid.

A still earlier paper (O. K. Rice, J. Am. Chem. Soc. 63, 3 (1941)) gave $d\ln\Theta/dV=0.10$ instead of the 0.18 used here. The low value of $d\ln\Theta/dV$ gives a value of da_0/da equal to about 1.9. This is obviously ridiculous, and may be added to the reasons already discussed for discarding these calculations.

[22] This examination was greatly facilitated by more detailed data very kindly sent me both by Dr. Gingrich and Dr. Lark-Horovitz. I wish to thank these investigators for their assistance in this matter.

and which had about 10.0 atoms under the first peak. One thus gets the impression that there is a sharp change between 89.2° and 91.8°, amounting almost to a transition. It seems very natural to suppose that this change in the atomic distribution would be associated with a change in the behavior of da_0/da with a. But if the transition takes place between 89.2° and 91.8° one would expect the break in the curve in Fig. 2 or Fig. 3 to take place at $a=4.07$ or 4.08 instead of around $a=4.04$. However, a closer examination shows that the change in the atomic distribution curve is actually more gradual than appears on the surface. A close scrutiny of Eisenstein and Gingrich's Fig. 10, and Lark-Horovitz and Miller's Fig. 2, allows us to make the following estimates of the density function $4\pi r^2\rho(r)$ at the maximum (that is, the height of the maximum) at the various temperatures: 84.35°K, 12.7; 89.2°K, 10.5; 91.8°K, 9.3. Also, we make the following estimate of the value of this function at the first minimum (first two temperatures), *or* the second maximum (last temperature): 84.35°K, 2.5; 89.2°K, 3.9; 91.8°K, 5.9. Thus, certainly within the limits of error, we can say that we have a gradual decrease of density at the first maximum, and at the next position, around 4.7A, a gradual increase in density. Just how suddenly the minimum appears to change into a maximum only a more closely spaced and very accurate series of experiments by a single investigator could show. It may be that the second peak, which at 84.35°K is around 5.3A, slides with increasing temperature into the position at 4.7A. In any event, at present the process looks like a gradual shift from a distribution resembling a distorted face-centered cubic lattice to one resembling a body-centered cubic lattice. This goes on all through the temperature range from near the normal freezing point of argon to 91.8° and beyond (from the work of Eisenstein and Gingrich it appears to continue on into the high temperature range), which means that the change starts when a is in the neighborhood of 4.03 or 4.04A. (It could start at a slightly higher, but presumably does not start at a much lower value of a, for the distribution at 84.35° resembles a face-centered cubic distribution about as closely as would

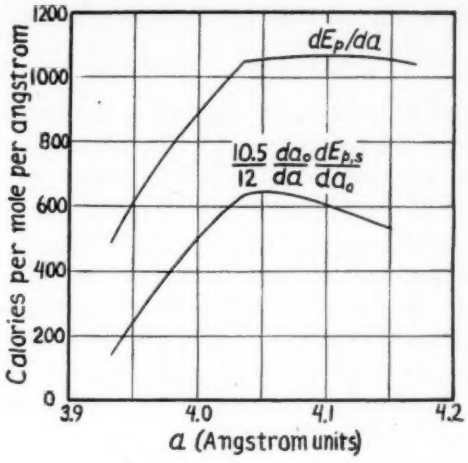

FIG. 4.

seem to be possible without having a definite lattice of that form). The apparently sudden change in coordination number between 89.2° and 91.8° is a psychological rather than a physical phenomenon. As soon as the minimum turns into a maximum, one divides the space around the central atom in a different way and relegates some of what were "nearest neighbors" to the class of "next-nearest neighbors."

If this interpretation of the atomic distribution curves is correct, it seems natural to associate the change in the slope of the curve da_0/da *vs.* a between $a=4.03$ and $a=4.04$ with the beginning of the appearance of traces of the distorted body-centered lattice at about the same value of a. In fact, off hand, one would not be surprised to see a discontinuity in da_0/da, but, according to the present picture, such a discontinuity would be associated with a discontinuity of $(\partial S/\partial V)_T$ or $(\partial P/\partial T)_V$, which would then occur at a definite volume independent of temperature, and this would be impossible by the theory of second-order transitions.

The Potential Energy of Liquid Argon

In Table V we have tabulated calculated values of dE_p/da. These can be correlated with the potential curve of the solid, as given in the preceding article. Since we believe that a_0 is to be identified fairly closely with the actual average interatomic distance of nearest neighbors in the liquid, we expect E_p to be related to the E_p for the solid at the given value of a_0. In fact, we

should be able to write, at least roughly,

$$E_p=(N/12)E_{p,s}(a_0)+E_d, \qquad (18)$$

where E_d is a constant, $E_{p,s}(a_0)$ is the potential energy of the solid at lattice distance a_0, and N is the average coordination number in the liquid.[23] If there is a "mixture" of face-centered and body-centered lattices in the liquid, we should perhaps add another adjective, and say that N is the effective average coordination number, as the next nearest neighbors in a body-centered lattice are close enough to have quite an influence on the central atom. If we differentiate Eq. (18) we obtain

$$dE_p/da=\tfrac{1}{12}(dN/da)E_{p,s}(a_0) +(N/12)(dE_{p,s}/da_0)(da_0/da). \qquad (19)$$

We may suppose that the greater portion of the variation of dE_p/da is in the last term of Eq. (19). Also the variation of N is probably not too large. Therefore, in the last term of Eq. (19) we have assumed N constant at 10.5. In Fig. 4 we have plotted dE_p/da from Table V and $(10.5/12)\times(dE_{p,s}/da_0)(da_0/da)$, taking $dE_{p,s}/da_0$ from the preceding article and da_0/da from Table V. It is seen that the two curves parallel each other in the region of small values of a, which may, at least for this region of a, be taken as confirmation of our point of view that information about the energy of the liquid may be obtained in a simple manner from the solid. It must be granted that we can only make this correlation because the somewhat arbitrarily chosen parameter a_0 lies within the range for which we have experimental data on the solid. In spite of this, we believe that the result must have at least qualitative significance.

The difference at small values of a between the two curves in Fig. 4, about 400 cal. mole^{-1} A^{-1}, gives the first term on the right-hand side of Eq. (19) and, since $E_{p,s}(a_0)$ is near 2000 cal. mole^{-1}, we find $dN/da=2.4A^{-1}$. This rate of change of N is small enough to justify our taking N constant[24] in the last term of Eq. (19); it may seem a little smaller than expected, but it is insensitive to the parameters. In any event, it can have a really objective significance in terms of the pictorial theory of the liquid only below a equal to 4.03 or 4.04A, where the lattice change begins to come in. For a greater than about 4.03A, it is seen that dE_p/da appears to be approximately constant, more so than $(N/12)(dE_{p,s}/da_0)(da_0/da)$. While we cannot ignore that the determination of $dE_{p,s}/da_0$ involves an extrapolation in this region, the greater degree of constancy of dE_p/da may be significant and explainable in the following way. Since the position of the first maximum of the distribution curve remains almost fixed,[13] the "percentage of body-centered structure," which must thus determine E_p, would be expected to be a linear function of a, at least over a small range. It is then not surprising if E_p is similar in this respect, and dE_p/da consequently nearly constant.

We now return to a discussion of the constant, or approximately constant, quantity E_d. The long range or translational type of motion, discussed in Section 1 above, in which the atoms slip around and exchange places, could not take place without changes in the distances between neighboring atoms. Thus the potential energy of the system cannot be the same as it would be if there were no such translational motion, and all neighboring atoms were at the same distance from each other. Even the translational motion will involve exchange of potential energy of certain pairs of molecules with other pairs, though the total potential energy in the entire large assemblage must always remain the same for any given a, and independent of temperature, if the motion is, in fact, to be properly described as translational. The energy E_d is the extra potential energy associated with the fluctuation in interatomic distances necessary for the translational motion to occur. E_d is always positive because the atoms are near a minimum of the mutual potential energy curve, i.e., in a region where it is concave upward.

From the available thermochemical energy we can estimate the total energy E of argon liquid at its freezing point. (This is reckoned on the basis of perfect gas at absolute zero having zero energy.) We can estimate E_t from Eq. (7). The difference $E-E_t$ is E_p; since we are dealing with the classical case we do not need to consider the

[23] Except for the constant E_d, which will be discussed later, this is essentially the assumption we have made previously (see reference 3).

[24] A correction would decrease the parallelism of the curves, but only slightly.

zero-point energy. E_d can then be estimated from Eq. (18). We find for argon liquid at its normal freezing point:

$$E=-1177 \text{ cal./mole},$$
$$E_t=398 \text{ cal./mole},$$
$$E_p=-1575 \text{ cal./mole},$$
$$E_d=167 \text{ cal./mole},$$

(assuming $N=10.5$, $a_0=3.85$, and $L=1.9$). It will be recalled that E_t itself contains some potential energy. The kinetic energy is equal to $\frac{3}{2}RT$ or 250 cal./mole, so the potential energy contributes 148 cal./mole to E_t, a quantity of the same order of magnitude as E_d.

Prefreezing Phenomenon

In Section 4 we have noted that the curves in Fig. 1 corresponding to low molal volumes have an "abnormal" slope at the low temperature end. This is reflected in Fig. 2, where it is seen that $(\partial S/\partial V)_T$ is "abnormally" great at low temperatures and small values of a. An indication of the reason for this apparent abnormality is found when we plot

$$(\partial E/\partial V)_T=T(\partial S/\partial V)_T-P$$

against a, as in Fig. 5. The curve for dE_p/dV is included for comparison, and it is seen that at 320°K the $(\partial E/\partial V)_T$ curve parallels it reasonably well, but at lower temperatures $(\partial E/\partial V)_T$ becomes very great at small values of a. The values of $(\partial E/\partial V)_T$ are subject to considerable uncertainty, because they are calculated as a relatively small difference, but the qualitative trend is unmistakeable.

The trend of the curves in Figs. 2 and 5 can be explained if we suppose that at the lower temperatures the system tends on compression to go to some special state of low entropy and, simultaneously, low energy. This leads one to speculate that we are dealing here with a prefreezing phenomenon, in which submicroscopic particles or crystalloids, having essentially the crystal structure of the solid, are formed in the liquid.

Such a phenomenon can, of course, occur only if the free energy of the entire system is thereby lowered. One might wonder why, if formation of what are essentially small particles of solid lowers the free energy, the system does not go the whole way, and form a large crystal. The answer is, of course, the entropy of mixing of the solid particles with the molecules of liquid. When the liquid (without crystalloids) and the solid have very closely similar free energies, this may be sufficient to turn the balance and stabilize the mixture. One would not expect such a system to be stable over a very extended range. In Figs. 1 and 2, curves are shown[25] which indicate the points at which solid and liquid are in equilibrium. It will be seen that the abnormal values of $(\partial S/\partial V)_T$ actually occur to a considerable extent in the metastable region, where the solid has a lower free energy than the liquid. Only over a rather small range is our hypothetical mixture important and stable. It is hoped that it may be possible in subsequent work to give a more quantitative discussion of these phenomena. In our earlier discussion of the gas of hard elastic spheres we noted the possibility that such a gas on compression would form regions in which the "atoms" are in a cubic-close-packed structure (see SLM, p. 14). In this case, however, the "atoms" do not have an attractive force field, and, furthermore, these groupings are associated with an increase in the entropy of the

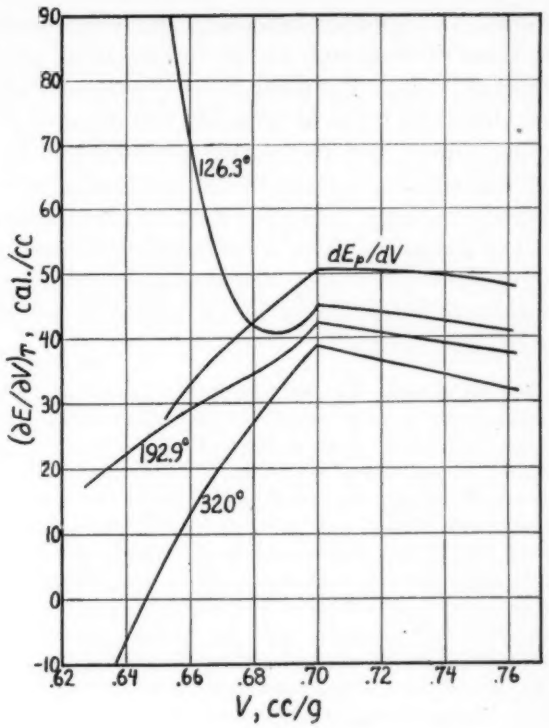

FIG. 5.

[25] In Fig. 2 the curve is merely indicated by the short vertical lines.

system. It appears, therefore, that this is not the same phenomenon as the "prefreezing" phenomenon we are discussing here. We may speculate that both types of grouping can occur in an actual liquid, the prefreezing phenomenon involving larger groups and being characterized also by a change in the interatomic distance to that of the solid, which is probably considerably larger than the average distance between closest neighbors in the liquid in the range in which prefreezing occurs.

The phenomena that we have here described as prefreezing were already noted in our earlier work.[3] The explanation given there, namely, that the decrease in entropy as the volume is decreased is associated with an increase in the average coordination number of the atoms of the liquid toward the coordinate number characteristic of solid argon, has some resemblances to and some points of difference from the explanation offered here. The process of prefreezing described in the above paragraphs will obviously be associated with an increase in average coordination number, but of a somewhat more specialized type than that envisaged in the earlier work. In particular, in the present discussion we conceive of the coordination number as varying appreciably in different regions which may be of appreciable size, whereas in the earlier work it was supposed that the average coordination number changed gradually with no appreciable local variations extending over considerable regions.

Conclusion

In concluding we may point out that perhaps the greatest advance recorded in this paper is the rather good correlation of the properties of the liquid with those of the solid. The attempt to use values of Θ taken directly from the solid appears to be successful. It is particularly interesting that it is absolutely essential to take into account the relaxation of the forces of the side-atoms in the liquid, and, in fact, as we have noted in Section 3, the liquid appears to be slightly more relaxed than our first estimate indicated. The correlation with the solid appears not only in the fact that the values of Θ for the solid give a good description of the properties of the liquid when proper account is taken of the interatomic distance, but also in the examination of the potential energy of the liquid and its comparison with that of the solid. Considerable uncertainty, unfortunately, still remains in the interpretation of the properties of the solid, since it does not appear to be possible to correlate Θ theoretically with the lattice distance. In the liquid we have a somewhat similar difficulty, since it requires recourse to the experimental data to correlate a_0 with a. Further progress in the understanding of the liquid will require solution of both problems. Since only one of them is actually characteristic of the liquid, the other belonging to the domain of the theory of the solid state, it now seems fair to say that our present understanding of the liquid has advanced to a point not too far behind our understanding of the solid.

Pressure Dependence of Accommodation Coefficients

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The pressure dependence of accommodation coefficients of gases on metals has been explained by assuming that the accommodation coefficient varies linearly with the fraction of the surface covered with adsorbed gas. It is further assumed that the accommodation coefficient has a negligibly small value α_0 on a gas-free surface and an asymptotic value α_∞ on a saturated surface. The assumptions lead to an accommodation coefficient isotherm which reproduces the pressure dependence of 119 accommodation coefficient values for ten gases on platinum with an average absolute deviation of 1.5 percent.

IT has long been recognized[1-8] that the accommodation coefficient of a gas on a metal surface depends upon the specific nature of the surface. Recently, values have been reported[8] for room temperature accommodation coefficients on platinum of ten gases over a wide range of pressure, so that sufficient experimental results are now available to test any theory which relates the value of the accommodation coefficient to characteristics of the surface which depend upon the gas pressure. It is the purpose of this paper to show that the observed variation of the accommodation coefficients with pressure can be explained quantitatively by considering the effect of adsorption on the metal surface. Although it frequently has been suggested[1-8] that adsorption is responsible for the increase in the value of the accommodation coefficient in changing from a gas-free to a gas-covered surface, no general functional relation has been proposed to date.

If we assume that the accommodation coefficient varies linearly with the fraction of the surface covered, the following relation holds:

$$\alpha=(1-\Theta)\alpha_0+\Theta\alpha_\infty, \qquad (1)$$

where α_0, α, and α_∞ are the accommodation coefficients at zero pressure, at the pressure at which the fraction Θ of the surface is covered, and at infinite pressure, respectively. Since we are dealing with gases adsorbed on relatively plane metallic surfaces at very low pressures and at temperatures far above the critical, we shall assume that the fraction of the surface covered is given by the simple Langmuir relation

$$\Theta=bp/(1+bp), \qquad (2)$$

where p is the gas pressure and b is a constant for a given gas and depends only upon the temperature. Equations (1) and (2) may be combined to give the following relation for the pressure dependence of the accommodation coefficient:

$$\alpha=\alpha_0+\frac{bp}{1+bp}(\alpha_\infty-\alpha_0)=\frac{1}{1+bp}\alpha_0+\frac{bp}{1+bp}\alpha_\infty. \qquad (3)$$

It will be assumed, for the present, that the magnitude of α_0 is sufficiently small so that it may be neglected in Eq. (3). This assumption is in accord with the available room temperature information shown in Table I which compares α_0 and α_∞ for several gases and metals. Although the

TABLE I. Comparison of room temperature values of α_0 and α_∞.

Gas	Metal	α_0	α_∞
Helium[a]	Platinum	0.03	0.403
Helium[b]	Platinum	0.07	0.403
Helium[c]	Nickel	0.07	0.403
Helium[d]	Tungsten	0.04	0.403
Neon[d]	Tungsten	0.05	0.700

[a] See reference 2 of text.
[b] See reference 6 of text.
[c] See reference 5 of text.
[d] See reference 4b of text.

[1] (a) J. K. Roberts, Proc. Roy. Soc. **A129**, 146 (1930); (b) **A135**, 192 (1932); (c) **A142**, 519 (1933).
[2] W. B. Mann, Proc. Roy. Soc. **A146**, 776 (1934).
[3] W. B. Mann and W. C. Newell, Proc. Roy. Soc. **A158**, 397 (1937).
[4] (a) W. C. Michels, Phys. Rev. **40**, 472 (1932); (b) **52**, 1067 (1937).
[5] B. Raines, Phys. Rev. **56**, 691 (1939).
[6] P. Rolf, Phys. Rev. **65**, 185 (1944).
[7] L. B. Thomas and F. Olmer, J. Am. Chem. Soc. **65**, 1036 (1943).
[8] I. Amdur, M. M. Jones, and H. Pearlman, J. Chem. Phys. **12**, 159 (1944).

TABLE II. Test of general relation $\alpha=[bp/(1+bp)]\alpha_\infty$.

Gas	α_∞	b (mm^{-1})	P (mm)	α_{obs}	α_{calc}	$100\left\|\frac{\Delta\alpha}{\alpha_{obs}}\right\|$
He	0.409	276	0.009639	0.300*	0.298	0.7
			0.01011	0.296	0.301	1.7
			0.04097	0.386	0.376	2.6
			0.05250	0.376	0.383	1.9
			0.06076	0.392	0.386	1.5
			0.07714	0.391	0.391	0.0
			0.09940	0.385	0.395	2.6
			0.1127	0.398	0.397	0.3
			0.1450	0.400	0.400	0.0
			0.1740	0.398	0.401	0.8
			0.1995	0.406	0.402	1.0
			0.2210	0.394	0.403	2.3
			0.2461	0.411	0.404	1.7
			0.2596	0.408	0.404	1.0
			0.2854	0.403	0.404	0.2
			0.3223	0.404	0.405	0.2
			0.3417	0.400	0.405	1.2
			0.3583	0.406	0.405	0.2
					Mean	1.1
Ne	0.718	165	0.01104	0.466	0.462	0.9
			0.01374	0.487	0.496	1.8
			0.04714	0.642	0.634	1.2
			0.06002	0.659	0.650	1.4
			0.1018	0.685	0.675	1.5
			0.1709	0.700	0.691	1.3
			0.2322	0.705	0.697	1.1
			0.2900	0.706	0.701	0.7
			0.3669	0.700	0.703	0.4
			0.3940	0.703	0.704	0.1
			0.4671	0.691	0.706	2.2
					Mean	1.1
A	0.870	195	0.01095	0.596*	0.596	0.0
			0.01312	0.612	0.627	2.5
			0.05125	0.807	0.793	1.7
			0.1045	0.833	0.831	0.2
			0.1589	0.851	0.844	0.8
			0.1643	0.847	0.845	0.2
			0.2157	0.848	0.852	0.5
			0.2252	0.856	0.852	0.5
			0.3015	0.853	0.857	0.5
			0.3497	0.845	0.859	1.7
			0.3883	0.842	0.860	2.1
					Mean	1.0
Kr	0.878	126	0.009823	0.445*	0.487	9.4
			0.04863	0.776	0.757	2.7
			0.06158	0.800	0.780	2.5
			0.1040	0.826	0.818	1.0
			0.1077	0.842	0.820	2.6
			0.1451	0.850	0.836	1.6
			0.1818	0.857	0.844	1.5
			0.2173	0.855	0.850	0.6
			0.2451	0.843	0.854	1.7
			0.2914	0.841	0.858	2.0
			0.3484	0.841	0.861	2.4
			0.3764	0.840	0.863	2.7
			0.4165	0.840	0.864	2.9
			0.4766	0.826	0.867	5.0
					Mean	2.8
Xe	0.881	206	0.007116	0.469*	0.522	11.3
			0.01127	0.736*	0.614	16.6
			0.03784	0.794	0.779	1.9
			0.06307	0.810	0.816	0.7
			0.07540	0.848	0.826	2.6
			0.1250	0.865	0.846	2.2
			0.1725	0.869	0.854	1.7
			0.2111	0.866	0.859	0.8
			0.2524	0.849	0.862	1.5
			0.2891	0.856	0.864	0.9
			0.3352	0.835	0.866	3.7
			0.3986	0.864	0.868	0.5
					Mean	3.7
H_2	0.316	545	0.008717	0.253*	0.261	3.2
			0.009725	0.270*	0.266	1.5
			0.04916	0.309	0.304	1.6
			0.1013	0.311	0.310	0.3
			0.1027	0.316	0.310	1.9
			0.1536	0.316	0.312	1.3
			0.2039	0.312	0.313	0.3
			0.2479	0.309	0.313	1.3
			0.3111	0.309	0.314	1.6
			0.3434	0.308	0.314	1.9
					Mean	1.5
D_2	0.396	697	0.01162	0.350*	0.353	0.9
			0.04888	0.388	0.385	0.8
			0.06222	0.386	0.387	0.3
			0.1041	0.395	0.391	1.0
			0.1056	0.392	0.391	0.3
			0.1439	0.394	0.392	0.5
			0.1767	0.398	0.393	1.3
			0.2048	0.399	0.393	1.5
			0.2112	0.396	0.393	0.8
			0.2903	0.389	0.394	1.3
			0.3470	0.389	0.394	1.3
			0.3804	0.387	0.395	2.1
			0.4148	0.385	0.395	2.6
					Mean	1.1
N_2	0.783	392	0.009121	0.620*	0.612	1.3
			0.01146	0.625	0.641	2.6
			0.04950	0.758	0.745	1.7
			0.09147	0.765	0.762	0.4
			0.1008	0.761	0.764	0.4
			0.1106	0.761	0.765	0.5
			0.1524	0.784	0.770	1.8
			0.2107	0.776	0.774	0.3
			0.2181	0.775	0.774	0.1
			0.2973	0.767	0.777	1.3
			0.3255	0.763	0.777	1.8
					Mean	1.1
CO	0.778	702	0.008454	0.665*	0.666	0.2
			0.05471	0.756	0.758	0.3
			0.09192	0.768	0.766	0.3
			0.1216	0.778	0.769	1.2
			0.1778	0.776	0.772	0.5
			0.2064	0.781	0.772	1.2
			0.2509	0.765	0.774	1.2
			0.3017	0.768	0.774	0.8
			0.3311	0.767	0.775	1.0
					Mean	0.7

TABLE II.—*Continued.*

Gas	α_∞	b (mm^{-1})	P (mm)	α_{obs}	α_{calc}	$100\left\|\frac{\Delta\alpha}{\alpha_{obs}}\right\|$
O_2	0.800	242	0.008557	0.534*	0.541	1.3
			0.05029	0.742	0.741	0.1
			0.09046	0.787	0.767	2.5
			0.1226	0.782	0.775	0.9
			0.1520	0.784	0.781	0.4
			0.2080	0.792	0.786	0.8
			0.2306	0.779	0.787	1.0
			0.2579	0.782	0.789	1.3
			0.3054	0.770	0.791	2.7
			0.3259	0.777	0.792	1.9
					Mean	1.3

α_∞ values are taken from measurements using a platinum wire,[8] they are assumed to be essentially independent of the wire used because of the saturation of the metal surface.

Inspection of Eq. (3) shows that the elimination of α_0 produces an extremely small effect on values of α calculated at pressures where an appreciable fraction of the surface is covered, since the small α_0 term is, under these conditions, multiplied by the term $1/(1+bp)$ which approaches zero as the surface approaches saturation. The simplified theoretical equation for the pressure variation of the accommodation coefficient will therefore be taken as

$$\alpha=\frac{bp}{1+bp}\alpha_\infty \tag{4}$$

or

$$1/\alpha=1/\alpha_\infty+1/(bp\alpha_\infty). \tag{5}$$

Values of b and α_∞ were computed from Eq. (5) for each gas listed in Table II from the observed accommodation coefficients at the tabulated pressures. The method of least squares was used with the standard weighting procedure[9] necessitated by the inversion of Eq. (4) to produce Eq. (5) which is linear in the reciprocals of the desired constants. The starred α_{obs} values differ from those originally published[8] because of a correction required in the original meter readings from which these values were computed. These readings fell on a different scale than the others and were found, upon calibration of the meter, to be in error by about 1 percent. This relatively small error has a large effect on the accommodation coefficients at the low pressures involved because of the small difference between the meter reading in vacuum and at the given pressure. The entries under α_{calc} were computed from Eq. (4) using the b and α_∞ values given in the table.

The agreement between the observed and calculated accommodation coefficients, as expressed by the absolute percentage deviations, seems quite satisfactory in all but three cases, the first value for krypton and the first two values for xenon. This may be caused by the difficulty of obtaining precise values of α_{obs} in these cases, where the low pressure and the low free molecule conductivity combine to give a very small difference between the energies required to heat the platinum wire to a given temperature in vacuum and in the gases at the recorded pressures. It is also possible, but less likely, in the opinion of the author, that these larger deviations result from the assumption that α_0 is negligible in comparison with α_∞ since, in this case, it would be difficult to explain the opposite sign of the deviations in the first two entries for xenon.

It is not possible to make a quantitative comparison between the results of Table II and those of other investigators who have determined accommodation coefficients on platinum, since only Rolf[6] and Thomas and Olmer[7] have published details which show that the heat flow problem has been properly analyzed, and in both cases only single values of the accommodation coefficient are reported for a wide range of pressure. Furthermore, the results of Thomas and Olmer, particularly those near unity, are uncertain because of an error in one of their formulas.[8] In Table III the accommodation coefficients reported by Rolf and by Thomas and

TABLE III.

Investigator	Gas	α_{obs}	P_{obs} (mm)	P_{calc} (mm)
Rolf	He	0.170	1×10^{-3} to 1×10^{-2}	2.6×10^{-3}
Thomas and Olmer	H_2	0.220	0 to 5×10^{-2}	5.0×10^{-3}
Thomas and Olmer	D_2	0.295	0 to 5×10^{-2}	4.2×10^{-3}
Thomas and Olmer	He	0.238	0 to 5×10^{-2}	4.2×10^{-2}
Thomas and Olmer	Ne	0.57	0 to 5×10^{-2}	2.4×10^{-2}
Thomas and Olmer	A	0.89	0 to 5×10^{-2}	
Thomas and Olmer	O_2	0.74	0 to 5×10^{-2}	4.9×10^{-2}

[9] J. B. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, 1930), p. 370ff.

Olmer have been combined with the constants of Table II to ascertain if the pressures calculated from Eq. (4) fell within the ranges cited by these authors.

The author feels that the qualitative agreement in six of the seven cases in Table III tends to support the present simple adsorption theory but that more reliable confirmation must await additional experimental results of the type given in Table II.

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Theory of the Non-Tetrahedral Carbon Atom

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The hybridization of s and p orbitals to give non-tetrahedral orbitals is discussed. The results are applied to cyclic hydrocarbons. For cyclopentane the theory yields an H-C-H angle of 111° 1′, and for cyclobutane an H-C-H angle of 180°.

THE method of directed valence bonds as developed by Pauling[1] is based on the following postulates. A single bond arises from the interaction of two unpaired electrons of opposite spin derived from different atoms. Of two orbitals in an atom the one which can overlap more with the orbital of another atom will form the stronger bond with that atom. The direction of this bond will be that direction in which the orbital wave functions of the two atoms overlap as much as possible. In applying these postulates to the carbon atom Pauling assumed that orbitals were formed from a combination or hybridization of s and p orbitals. The hybridization was made in such a way as to yield the maximum bond strengths.

HYBRIDIZATION IN THE NON-TETRAHEDRAL CARBON ATOM

Let us now consider how this theory is to be altered if we specify one of the valence angles of the carbon atom. Such a restriction is present in compounds such as cyclopropane, cyclobutane, and cyclopentane. It will be assumed that a certain amount of symmetry exists. Thus numbering the bonds of carbon as 1, 2, 3, and 4, it will be assumed that bonds 1 and 2 are equivalent and that bonds 3 and 4 are equivalent.

[1] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931). See also W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927); J. C. Slater, Phys. Rev. **37**, 481 (1931).

It is assumed that the radial parts of the wave functions ψ_s, ψ_{p_x}, ψ_{p_y}, ψ_{p_z} are so similar that their differences are negligible. The angular parts, normalized to 4π, are given by the equations

$$s=1, \tag{1}$$

$$p_x=\sqrt{3}\sin\vartheta\cos\varphi, \tag{2}$$

$$p_y=\sqrt{3}\sin\vartheta\sin\varphi, \tag{3}$$

$$p_z=\sqrt{3}\cos\vartheta, \tag{4}$$

where ϑ and φ are the angles used in polar coordinates.

The angular part of each of the bond-forming eigenfunctions is approximated by functions of the form

$$f_i=a_is+b_ip_x+c_ip_y+d_ip_z, \tag{5}$$

where i is 1, 2, 3, or 4. The coefficients a_i, b_i, c_i, and d_i are determined by the normalization condition

$$a_i^2+b_i^2+c_i^2+d_i^2=1, \tag{6}$$

and by the orthogonality condition

$$a_ia_j+b_ib_j+c_ic_j+d_id_j=0, \quad i\neq j. \tag{7}$$

The direction of the maximum of the first bond eigenfunction is arbitrary. It is chosen to lie along the x axis. Hence

$$f_1=a_1s+(1-a_1^2)^{\frac{1}{2}}p_x, \tag{8}$$

where b_1 has been replaced by $(1-a_1^2)^{\frac{1}{2}}$ so that Eq. (6) might be satisfied.

The direction of the maximum of the second bond eigenfunction can without loss of generality be chosen to lie in the xz plane. Thus

$$f_2 = a_2 s + b_2 p_x + d_2 p_z. \tag{9}$$

From Eq. (6)

$$a_2^2 + b_2^2 + d_2^2 = 1. \tag{10}$$

From Eq. (7)

$$a_1 a_2 + b_1 b_2 = 0. \tag{11}$$

Since bonds 1 and 2 are assumed to be equivalent bonds

$$a_2 = a_1. \tag{12}$$

Hence

$$b_2 = -[a_1^2/(1-a_1^2)^{\frac{1}{2}}], \tag{13}$$

and

$$d_2 = [(1-2a_1^2)/(1-a_1^2)]^{\frac{1}{2}}. \tag{14}$$

In a similar way it is found that

$$a_3 = a_4 = (\tfrac{1}{2} - a_1^2)^{\frac{1}{2}}, \tag{15}$$

$$b_3 = b_4 = -a_1\{[(1-2a_1^2)/(2(1-a_1^2))]^{\frac{1}{2}}\}, \tag{16}$$

$$c_3 = -c_4 = 1/\sqrt{2}, \tag{17}$$

$$d_3 = d_4 = -a_1/[2(1-a_1^2)]^{\frac{1}{2}}. \tag{18}$$

Now let us relate the direction of the maximum of the second bond eigenfunction to the value of a_1. First substitute Eqs. (1), (2), (4), (12), (13), and (14) in Eq. (9). Then let $\varphi = 180°$ and differentiate f_2 with respect to ϑ. Setting this derivative equal to zero then gives the result

$$\tan \vartheta = a_1^2/(1-2a_1^2)^{\frac{1}{2}}. \tag{19}$$

Since the direction of the maximum of the first bond eigenfunction lies along the x axis, the angle between the two maxima equals $90° + \vartheta$.

CYCLOPENTANE

It is assumed that all the carbon atoms in cyclopentane lie in a plane and form a symmetrical ring. Also it is assumed that the directions of the bonds coincide with the directions of the maxima of the bond eigenfunctions. Consider one carbon atom in the ring and choose the coordinate axes so that f_1 and f_2 represent the angular part of the eigenfunctions which form the bonds with the neighboring carbon atoms. The value of a_1 can be obtained using Eq. (19) and taking $\vartheta = 18°$. The value of a_3 is then calculated using Eq. (15). Now consider the axes rotated so that the direction of the x axis coincides with the direction of a C-H bond. The new value of a_1 is equal to the value of a_3 in the old coordinate system. The value of the H-C-H angle can now be calculated using Eq. (19). The final result is

$$\measuredangle \mathrm{HCH} = 111° 1'. \tag{20}$$

It is evident that this value differs appreciably from the tetrahedral angle 109° 28′.

CYCLOBUTANE

If a_1 is taken equal to zero, it is found by Eq. (19) that ϑ equals zero and hence the angle between the directions of the maxima of f_1 and f_2 equals 90°. Proceeding as before one obtains

$$\measuredangle \mathrm{HCH} = 180°. \tag{21}$$

CYCLOPROPANE

The calculations of Herzberg[2] seem to support the view that the HCH angle in cyclopropane is a straight angle. This indicates an electronic structure similar to that described for cyclobutane. However now the directions of the maxima of f_1 and f_2 would not coincide with the C-C bond directions. Instead there would be a difference of 15° between each C-C bond and the maximum of f_1 and f_2, respectively.

DISCUSSION

The results obtained are to be regarded as rough approximations. The principal effect neglected is probably the repulsion between different groups in the molecule. In the case of cyclobutane the HCH angle is probably altered considerably by the repulsion between the hydrogen atoms and the neighboring carbon atoms.

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[2] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

Surfaces of Solids XVII

A First- and a Second-Order Phase Change in the Adsorbed Film of *n*-Heptane on Graphite*

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and

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The films of *n*-heptane formed by adsorption on the surface of graphite between 25° and 40°C exhibit a first- and a second-order phase transition. The first-order transition occurs between the gaseous and liquid expanded phases. The second-order transition occurs between the liquid expanded and liquid intermediate phases, and between the gaseous and liquid intermediate phases above the critical temperature. Since the behavior of the film is the same as that observed with insoluble films on aqueous subphases, the nomenclature for the latter is used. The critical constants for the gaseous film were determined as: temperature, 31°C; area, 400A² per molecule; and film pressure, 1.05 dyne cm⁻¹. These values are different from those found for *n*-heptane on ferric oxide, which shows that the solid as well as the gas plays an important role in the determination of the adsorption isotherm. The heat of transition for the first-order change is estimated as 13,000±5000 cal. mole⁻¹ at 25°C. It is found at corresponding temperatures, within this large experimental error, that the heat evolved in the first-order transition is the same on graphite and ferric oxide.

I. INTRODUCTION

RECENTLY, the writers have presented experimental evidence which shows that films formed by adsorption on the surfaces of solids may undergo first-order phase transitions on increase of pressure from the gas phase. These are analogous to those which occur in insoluble films on an aqueous subphase. Data were presented for two systems: *n*-heptane on silver[1] and *n*-heptane on ferric oxide.[2]

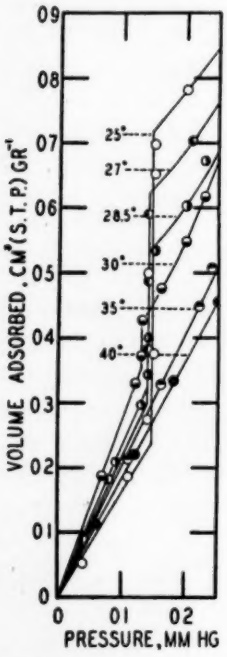

FIG. 1. The isotherms between 25° and 40°C of *n*-heptane on oxygen-free graphite with less than 0.004 percent ash to pressures of 0.025 mm. At 25°, 27°, 28.5°, and 30°C the isotherms exhibit a discontinuity in the volume adsorbed as a function of the pressure. This indicates a first-order phase transition of the film.

Of the two systems, that which involves ferric oxide was the more extensively investigated. The system exhibited all the critical temperature phenomena in the film pressure (π)-area (σ) relationships associated in general with a first-order transition. It was also shown that the compressibility κ of the film formed by adsorption on the surface of the solid is

$$\kappa = \frac{V_M \Sigma}{RTv^2}\left(\frac{\partial v}{\partial \ln p}\right)_{T,\Sigma},$$

where V_M is molar gas volume at standard temperature and pressure; Σ, the specific area of the solid; R, the gas constant; T, the absolute temperature; v, the volume of gas adsorbed per gram of solid; and p, the equilibrium pressure. From the criteria for phase changes in films presented by Dervichian[3] and by Harkins and

* The writers wish to acknowledge the helpful cooperation in this work of Dr. Orlan M. Arnold of the Chrysler Corporation. This is a part of a larger research project under the general direction of William D. Harkins.

[1] G. Jura, E. H. Loeser, P. R. Basford, and W. D. Harkins, J. Chem. Phys. **13**, 535 (1945).
[2] G. Jura, E. H. Loeser, P. R. Basford, and W. D. Harkins, J. Chem. Phys. **14**, 117 (1946).
[3] D. G. Dervichian, J. Chem. Phys. **7**, 931 (1939).

Boyd[4] it also was shown that for a first-order transition $(\partial v/\partial \ln p)_{T,\Sigma}$ becomes infinite, while for a second-order transition there is a finite discontinuity in the derivative.

In the present paper, which considers the adsorption of *n*-heptane on graphite at low relative pressures, the experimental data indicate that both a first- and a second-order transition occur at pressures below 0.040 mm at temperatures between 25° and 40°C.

II. EXPERIMENTAL METHODS AND MATERIALS

The experimental procedures and materials used have been fully described in previous papers.[5,6] The graphite used is that which contains less than 0.004 percent ash. It was furnished by the courtesy of Dr. Lester L. Winter of the National Carbon Company. As in the previous paper, 4.22 m^2g^{-1} was used as the area of the sample, as obtained from an absorption isotherm of nitrogen at −195.6°C, and calculated by the relative method of Harkins and Jura.

III. EXPERIMENTAL RESULTS

The adsorption isotherms of *n*-heptane on graphite are exhibited in Fig. 1. These were obtained at pressures up to 0.025 mm at 25.00° ±0.02, 27.00°±0.02, 28.50°±0.02, 30.00°±0.02, 35.00°±0.05, and 40.00°±0.05C. At 25°, 27°, 28.5°, and 30°C, the isotherms exhibit a first-order phase change at a pressure of 0.014 mm Hg. The behavior of the isotherms in this region is exactly analogous to that of those observed when ferric oxide is the subphase. The best values for the critical constants on graphite are: $T=31$°C, $\sigma=400$A² per molecule, and $\pi=1.05$ dyne cm^{-1}. The corresponding values for ferric oxide are: $T=29$°C, $\sigma=900$A² per molecule, and $\pi=0.45$ dyne cm^{-1}. These two sets of values show the dependence of the critical constants on the nature of the subphase. Obviously, the critical constants must depend also on the nature of the gas.

The heat evolved in the first-order transformation of the film of *n*-heptane on graphite at 25°C is estimated at 13,000±5000 cal. $mole^{-1}$, which is practically the same as that on ferric oxide at the same temperature: 12,000±5000 cal. $mole^{-1}$. If the comparison were made at corresponding temperatures for the film on graphite and ferric oxide, the heats evolved in the phase transformation would be the same. The experimental facts seem to indicate that the gas-gas interaction cannot be neglected, even when the adsorbed molecules are separated by comparatively large distances.

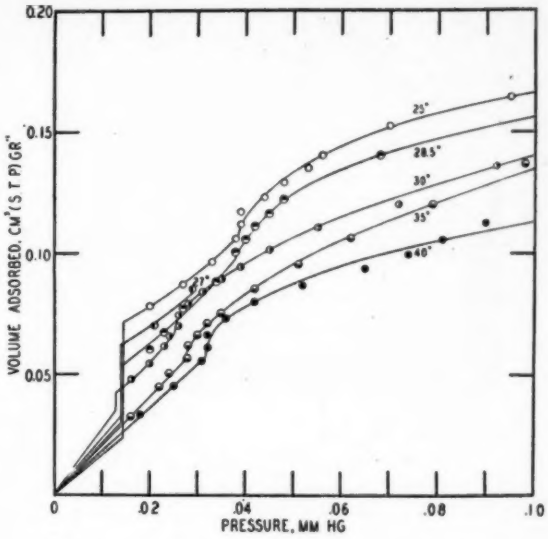

FIG. 2. The same as Fig. 1, but to pressures of 0.100 mm Hg. These curves exhibit at pressures above 0.025 mm a second-order phase transition of the film.

Figure 2 exhibits the isotherms to a pressure of 0.100 mm. The experimental points for the discontinuity and lower pressures have been omitted, since they are shown in Fig. 1. Each of these curves (except that at 27°C, where the data are insufficient) exhibits a sudden increase in $(\partial v/\partial p)_{T,\Sigma}$ at pressures decreasing from 0.038 mm at 25°C to 0.025 mm at 30°C and then again increasing to 0.032 mm at 40°C. The data in this region are completely reproducible, and the values do not change with time. In several of the determinations in this region two consecutive points are found at the same pressure. It is apparent that this rapid change in $(\partial v/\partial p)_{T,\Sigma}$ represents a second-phase change in the film. The isotherms below the critical temperature ($T\leqq30$°C) cannot be used to decide this point, since too few experimental points can be ob-

[4] W. D. Harkins and G. E. Boyd, J. Phys. Chem. **45**, 20 (1941).
[5] G. Jura and W. D. Harkins, J. Am. Chem. Soc. **66**, 1356 (1944).
[6] W. D. Harkins, G. Jura, and E. H. Loeser, J. Am. Chem. Soc. **68**, 554 (1946).

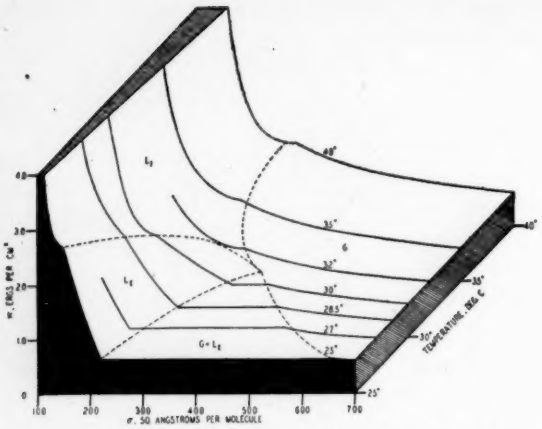

FIG. 3. A cabinet projection of the $\pi-\sigma-T$ surface of the film of *n*-heptane on graphite. In this projection the correct $\pi-\sigma$ relations are maintained. The temperature axis is drawn at 45°. Thus, an increase of 5°C causes an apparent increase of molecular area of 100A² per molecule and an apparent increase of 1 dyne cm^{-1} in the film pressure. The surface shows four regions: (1) the gas, G; (2) the "liquid expanded," L_E; (3) the "liquid intermediate," L_I; (4) the two-phase region, gas+"liquid expanded."

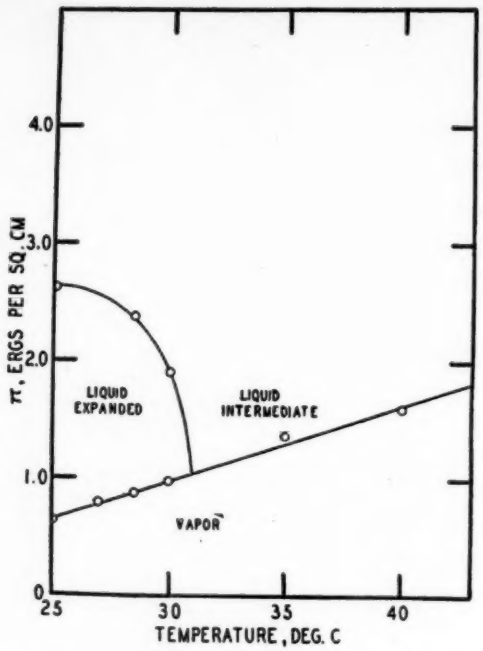

FIG. 4. The $\pi-T$ phase diagram of the film of *n*-heptane on graphite. The triple point is placed at the critical temperature and critical film pressure.

tained between the identified first-order transition at 0.014 mm and the possible second transition. At 35° and 40°C, however, a definite decision can be made. At these temperatures a study of the data shows that a transition does occur, the question being solely one of order, i.e., first or second. The fact that in some cases two points are observed at the same pressure might indicate a first-order change with an exceedingly small change of area. A study of the pressure (π)-area (σ) curves indicates, however, that the only reasonable assumption is that a second-order change occurs. If the transition were first order, the compressibility of the phase formed by the transition would at first decrease and then increase as the pressure is increased. This behavior is unreasonable from both the two- and three-dimensional behavior of matter under pressure. This difficulty is obviated if it is assumed that order of the change is second rather than first. The $\pi-\sigma$ curves are exhibited in Fig. 3.

If the second transition is considered as first order, the heat relations on this basis are peculiar. The ΔH for the second transition on the assumption that the change is first order, becomes positive below the critical temperature and negative above this temperature. Also, at 25° $\Delta H=300$ cal. $mole^{-1}$, which increases to 27,000 cal. $mole^{-1}$ at 30°C and decreases to −700 cal. mole at 35° and 40°. The ΔH for the process of transforming the vapor to the third phase that appears would be −12,000 cal. $mole^{-1}$ at 25°C, which would increase to 26,000 cal. $mole^{-1}$ at 30°C and then at above the critical temperature change to −700 cal. $mole^{-1}$. This behavior is also unlikely. Thus, it is almost certain that the phase change under consideration is of the second order. The fact that this change exhibits an appearance somewhat analogous to a change of the first order is presumably due to an insufficient sensitivity of the pressure measurements.

By analogy with the behavior of insoluble films on water, the phase formed from the gas by the first-order change would be the liquid expanded (L_e), while that formed by the second-order change from the gas and the analog of the liquid expanded would be considered the liquid intermediate (L_i) phase. The phase diagram of this system is given in Fig. 4. The diagram is in complete accord with our present knowledge of the behavior of films and also of matter in three dimensions, when the pressure, temperature, area (or volume) relations are considered.

Figure 4 does not represent all of the phases which appear in this system. At 25°C, where the

entire isotherm has been determined, the "liquid intermediate" phase transforms into a condensed phase at a film pressure of about 20 dyne cm^{-1}. The nature of this transition has not as yet been determined.

The second-order change reported here has also been found with other solids when *n*-heptane is the adsorbate, and also with *n*-butane and triptane at 0°C on several solids. The work done to date with *n*-butane indicates that the observed phenomena are the same as those found for graphite above the critical temperature. The work of Orr[7] strongly suggests that similar transformations take place when argon, nitrogen, and oxygen are adsorbed on ionic solids at temperatures in the neighborhood of 77°K. The writers are planning to repeat his work and, by taking more points, to determine whether or not these are phase transitions of the second order in the low pressure region. First-order transitions with nitrogen at these temperatures have been observed.

The results with graphite show, even when the adsorbed film is above the critical temperature of the liquid expanded film, that the increase of the pressure of the film transforms the gas into a phase which, below the critical temperature, does not appear until much higher pressures are attained. This behavior has its counterpart in the solidification of helium and other gases above their critical temperatures. Thus, in films formed on the surfaces of solids by adsorption, phase transformations from the gas are possible, even above the critical temperature of the liquid expanded.

[7] W. J. C. Orr, Proc. Roy. Soc. London **173A**, 349 (1939).

Errata: Statistical Mechanics of Transport Processes

I. General Theory

[J. Chem. Phys. **14**, 180 (1946)]

JOHN G. KIRKWOOD
Baker Laboratory, Cornell University

IN this article an important distinction was made between the distribution function $f^{(n)}(\mathbf{p}, \mathbf{q}; t)$ at time t and its time average $\bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t)$ over an interval τ subsequent to the instant t. The two functions are related in the following manner,

$$\bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t) = \frac{1}{\tau} \int_0^\tau f^{(n)}(\mathbf{p}, \mathbf{q}, t+s) ds.$$

Unfortunately, serious confusion was caused by a series of typographical errors introduced between galley and page proof, in which the bar was omitted at random from the functions $\bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t)$. These errors are to be corrected as follows:

1. $\bar{f}^{(N)}$ to replace $f^{(N)}$ on the left side of the second of Eqs. (14).
2. $\bar{f}^{(n)}$ to replace $f^{(n)}$:
   (a) On left side of second of Eqs. (20).
   (b) In integrand of Eq. (21).
   (c) On left side of the third of Eqs. (46).
   (d) On left side of the differential equation, Eq. (47).
   (e) On right side of the first of Eqs. (48).
3. $\bar{f}^{(1)}$ to replace $f^{(1)}$:
   (a) In the integrands on the right sides of Eqs. (23), (24), (25), (26), and the second of Eqs. (60).
   (b) On the left side of the differential equation, Eq. (49).
   (c) On both sides of the differential equation, Eq. (59).
   (d) First sentence, last paragraph, page 194.

Two additional errors of a minor character are also to be noted:

4. In the first of Eqs. (70), C_l, the concentrations in moles/cm^3 should replace C_l, the concentrations in molecules/cm^3.
5. The expression $6\pi\eta\mathbf{p}_i/m_i$ should replace $6\pi\eta m_i\mathbf{p}_i$ at the end of the eighteenth line from the bottom of the second column, page 198.

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

On the Weak Associations in Water and in Aniline

R. PARSHAD
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January 22, 1946

PAULING'S concept of the hydrogen bond has explained a vast field of experimental data.[1] In this note we wish to show that his concept can be further used to explain the very interesting property of the comparative weakness of associations in water. For example, taking the energy of the hydrogen bond as the thermal energy required to rupture it, the energy of the hydrogen bond in water is 4.5–5 kcal./mole, compared to that of 6 kcal./mole for alcohols and 7–8 kcal./mole for carboxylic acids. It is probably not well realized that the "abnormal" properties of water are not only caused by its vast network of associations, but also because these associations are weak. It is not the mere presence of hydrogen bonds but their progressive breaking with increase of temperature, or pressure etc., which causes the open structure of water caused by extensive hydrogen bonding to crumble and bring in the abnormal properties. For that matter, carboxylic acids are hardly abnormal in the liquid states. Because of the nearly non-breaking of the strong dimers, the latter behave as single molecules until even vaporization. Indeed the vapor state rather than the liquid state of these acids may be called associated in the sense that water is in the liquid state.

While the extensive nature of the association in water may be explained as caused by favorable steric factors, (*viz.* all atoms in a state to be engaged in hydrogen bonds, the donating power of O in terms of H's to be equal to the accepting power, and the ability to be able to form hydrogen bonds on all sides (tetrahedral bonding), etc., the weak nature of these associations may be explained as follows.

According to Pauling, in the O−H valency link, there is resonance between the covalent state and the ionic state. A pair of electrons is at one time shared between O and H (covalent state) and in the next instant is all attracted on to O by its electronegativity, leaving the H a bare proton (ionic state). In the state of the ionic character of O−H, the proton H attracts and is attracted by an O of another O−H in virtue of the latter's total negative charge (when in the ionic state) and any unpaired electron pairs on it.

Here we consider two factors:

(1) As one O−H link of a water molecule is ionic, the O is negative, because of the pair of electrons that it has attracted on to itself. This negative charge on O will discourage the attraction of another pair of electrons from the other O−H link. In other words, the negative charge on O, formed because of the ionic character of O−H link, decreases the electronegativity of O and so the ionic character of the second O−H link. As both the O−H links are of course indistinguishable, this means that the ionic character of both the O−H's are reduced, and so the hydrogen bonds formed will be weak. The liquids like alcohols have one H to one O and so do not suffer this weakening of the ionic character.

(2) Consider the effect of an H, on O, not of its own valency link but that with which it is involved in a hydrogen bond.

O—H - - - - - - - - - O—H

In the above figure, the atoms concerned are in bold face. The **H** proton will attract electrons on **O**, and so the latter will increase its effective nuclear charge for its own H (on the right of the figure). The electronegativity of O is increased and so the ionic character of O−H, leading to increase of hydrogen bonding power.

The effects of (1) and (2) run in counter directions but evidently the effect of factor (1) is greater than that of (2), as in the former the mutual effect of O and H in the same valency link is considered. We may note here that derivation of factor (2) is contrary to that of Pauling.[2] According to him the O−H link concerned is strengthened (or its ionic character decreased). However, Pauling's derivation all the more supports the inference of weak associations in water.

The above considerations for water can also be used to explain why aniline containing an amino group forms no or very little hydrogen bonds, when it is also considered that N has lower electronegativity than O, and because of the extra phenyl group on N, lower number of unshared pair of electrons are left on N for attraction by a distant proton for forming a hydrogen bond. But the electron attracting property of the phenyl group itself will contribute some additional electronegative power to N, and because of this aniline may be more associated, if at all, than ammonia.

[1] L. C. Pauling, *Nature of the Chemical Bond* (Cornell University Press, New York, 1940).
[2] Reference 1, p. 326.

A Note on Communal Entropy. Remarks on a Paper by Henry S. Frank[1]

O. K. RICE
University of North Carolina, Chapel Hill, North Carolina
April 8, 1946

IN a recent series of interesting papers, Frank has discussed what he aptly calls the pictorial theory of the liquid state. These papers included, also, some consideration of the solid state, and the gas of hard elastic spheres.

In the latter discussion, Frank[1] has come into conflict with some statements previously made by me.[2] On page 487 of reference 1, Frank discusses the communal entropy of a closely packed three-dimensional gas of hard elastic spheres. This I had estimated as $3R$ per mole on the basis of Eq. (2) of reference 2. Frank rejects my Eq. (2) and substitutes his Eq. (36), but grants that the latter is not itself satisfactory. My equation, applied first to a *simple* cubic array, rests on the assumption that motions in the three directions of space are independent of each other, provided the system is sufficiently closely packed. Thus if an atom A (hard elastic sphere) is displaced out of the line joining its two neighbors, B and C (Fig. 1), it is assumed that its motion along this line is unaffected. This is true if the displacement is small enough. But even if the atoms are densely packed, large fluctuations become appreciably probable if the number of atoms in the line is large. It is, therefore, necessary to place some *arbitrary* restriction on the total possible displacement of any atom, allowing it to be not greater than some finite multiple (which may, of course, be as large as we please, if the spheres are sufficiently densely packed) of the average distance between atoms. Some such condition is necessary in order to keep the system in the assumed simple cubic lattice; if left to itself, the system would presumably tend to go over to a lattice of the face-centered cubic, or some related type, which would have a greater entropy; but this is not the problem we are attempting to solve. Even though the simple cubic lattice is not a stable lattice unless some restrictions are placed on the motions of the atoms, it is still useful to consider it, because it may be used as a guide to the cases which have a greater resemblance to physical reality.

Let us consider a sufficiently closely packed simple cubic array of N hard elastic spherical atoms packed in a cube of length l. Letting $K=(2\pi mkT/h^2)^{3N/2}$, the total partition function of this system will be given, assuming classical statistics, by[3]

$$Q^N=K\int\int\cdots\int dx_1dx_2\cdots dx_Ndy_1dy_2\cdots dy_Ndz_1dz_2\cdots dz_N. \quad (1)$$

In evaluating the integral we allow the x's, y's, and z's to take all possible values, keeping, however, each numbered atom in its particular place in the array. This latter condition makes it unnecessary to divide by $N!$, since we do not allow exchange of atoms. Since motions in the three

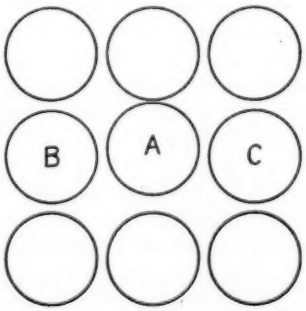

FIG. 1.

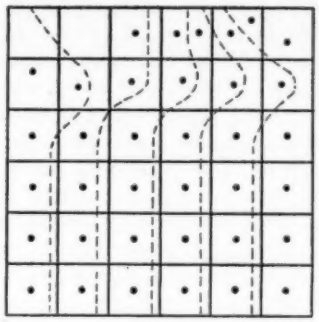

FIG. 2.

directions of space are independent, we may separate the x, y, and z parts of the integration, and since these parts are exactly alike, we may write

$$Q^N=K\left(\int\int\cdots\int dx_1dx_2\cdots dx_N\right)^3. \quad (2)$$

The integral consists of integrations along $N^{\frac{1}{3}}$ exactly similar rows of $N^{\frac{1}{3}}$ atoms each. Hence

$$Q^N=K\left(\int\int\cdots\int dx_1dx_2\cdots dx_{N^{\frac{1}{3}}}\right)^{3N^{\frac{1}{3}}} \quad (3)$$

Except for the restrictions on large displacements this integral is just that evaluated by Tonks.[4] It is clear from pages 4 and 5 of reference 2 that reasonable restrictions can be placed on the fluctuations without appreciably altering the value of this integral. We, therefore, insert Tonks' value with the appropriate changes ($N^{\frac{1}{3}}$ for N), obtaining

$$Q^N=K[(l-N^{\frac{1}{3}}\sigma)^{N^{\frac{1}{3}}}/N^{\frac{1}{3}}!]^{3N^{\frac{1}{3}}} \quad (4)$$

where σ is the diameter of the spheres. If $N^{\frac{1}{3}}$ is large enough $1/N^{\frac{1}{3}}!=e^{N^{\frac{1}{3}}}(N^{\frac{1}{3}})^{-N^{\frac{1}{3}}}$, excluding a factor whose logarithm will be negligible. Letting $v=l^3/N$ be the volume per atom, and setting $\theta=\sigma^3/v$, the expression becomes

$$Q^N=Ke^{3N}v^N(1-\theta^{\frac{1}{3}})^{3N}, \quad (5)$$

entirely equivalent to Eq. (2) of reference 2. As noted in reference 2, this is greater by the factor e^{3N} than the partition function which would be obtained if each sphere were confined to its own cell, the cells being all equal in size and completely filling the space. The molal communal entropy is, therefore, $3R$. How to take care of the case where the spheres are packed in a cubic close-packed (cubic face-centered) type of arrangement, rather than simple cubic, is probably sufficiently indicated in reference 2. This involves a certain estimate, rather than a rigorous straight-forward deduction, but it is undoubtedly a good estimate and, in any event, in itself, it in no way affects the communal entropy. The change to the cubic face-centered type may, on account of the blocking of fluctuations, have a slight effect on the communal entropy, somewhat similar to the effect due to restricting the size of the fluctuations in the simple cubic array.

While this seems to settle the problem from a formal mathematical point of view, it may be possible to bring out the difference between a closely packed aggregate of

spheres and a dilute gas, for which the communal entropy per mole is only R, more graphically. If the spheres are very densely packed, under the restrictions noted above a sphere cannot get out of its row and column. (For convenience we restrict ourselves to two dimensions.) On the other hand, consider the situation which may arise in the case of point atoms, as illustrated by Fig. 2. This figure shows a square divided into cells by solid lines, one cell for each atom. If we assume that the atoms may pass the cell boundaries, we can get a situation such as shown in Fig. 2. This may be considered as produced in the main by fluctuations in the top row only. It can also be produced by another set of fluctuations as is indicated by the broken lines. Since the two sets produce indistinguishable configurations, they give rise to only one state of the system. In the case of closely packed spheres, however, the two sets of fluctuations, if they were of the same order of magnitude relative to the free space (therefore taking the molecules out of their individual cells), would, nevertheless, give only small displacements relative to the diameter of the spheres. The two sets of small displacements would give rise in this case to distinguishable configurations. It is, therefore, seen that the closely packed spheres can have a greater communal entropy than the dilute gas, because in the latter case row and column fluctuations interfere and overlap, giving rise to indistinguishable configurations.

Frank has quite properly called attention to the arbitrary nature of communal entropy. It depends upon the size of the "natural" cell which one chooses in the first place, when one assumes that each atom is assigned to its own cell. However, it is agreed that, insofar as possible, the cells should be assigned so that they are of equal size, and completely fill the space available. Then the assignment is easy in the case of a densely packed gas of hard elastic spheres. When the atoms exert forces on each other, it becomes a little more difficult. I made an estimate of communal entropy in this case because I wished later to combine the partition function for a gas of hard elastic spheres with that of a Debye solid in setting up the partition function for a liquid, assuming each part carried its own communal entropy factor. It seemed reasonable to do this if the excitation of communal entropy was comparable in the two cases. Otherwise some special means of averaging might have been necessary. Though the Debye solid was found to have a communal entropy only 77 percent as excited as the dense gas of hard spheres, this did not seem sufficiently different to render any special computation necessary.

In order to make a fair comparison of the communal entropy in the two cases, it seemed necessary to define the "natural" cell for a Debye solid in a manner as nearly analogous as possible with the definition for the hard elastic spheres. If, in the hard-sphere case, all atoms are fixed in position except one, this one has a free volume 2^3 times as large as if it were confined to its own cell. It was, therefore, assumed that if all the atoms of a Debye solid were held fixed except one, this one also would move in an effective volume equal to 2^3 times its natural cell. It is known that this atom would vibrate with the root-mean-square value of the frequencies of the normal modes. Therefore, it seemed reasonable to say that a solid in which all atoms moved with this same mean frequency (Einstein model) was one in which the molal entropy was $3R$ ln 2 times as great as it would be if each atom were confined to its "natural" cell, and the communal entropy of the Debye solid was calculated by comparison with the Einstein model, on this basis. In any event, it seems more "natural" to me to define the "natural" cell by means of an average frequency. Frank prefers the Debye maximum frequency, which seems "artificial" to me. However, nothing can be proved about this. I merely wish to emphasize that I had a real reason for choosing the natural cell as I did in view of the purpose I had in mind.

Errata to reference 2. On page 3 of reference 2 (last sentence beginning in the first column) where it reads, "If this result is multiplied by the momentum integral and divided by h," replace h by h^N. This gives what we have called Q^N (though in this case it is for a one-dimensional array) and Q (correctly given by Eq. (1) of reference 2) is the partition function referred to a single atom.

At the end of page 6 and beginning of page 7, it was inadvertently stated "that the partition function per molecule of a Debye solid is $e^{\frac{1}{2}}kT/h\nu_m$." This is the partition function *per degree of freedom* and was used as such.

[1] H. S. Frank, J. Chem. Phys. **13**, 478 (1945).
[2] O. K. Rice, J. Chem. Phys. **12**, 1 (1944). For some errata see *ibid.* **12**, 521 (1944) and the end of this article.
[3] Q^N is called Q by Frank; to be consistent with my own Eq. (2) I retain Q for the partition function referred to a single atom.
[4] L. Tonks, Phys. Rev. **50**, 955 (1936).

Postscript to the Foregoing Note by O. K. Rice

HENRY S. FRANK
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April 8, 1946

I GREATLY appreciate the opportunity to see Professor Rice's "Note on Communal Entropy" in advance of publication, and to place on record as promptly as possible my agreement with the derivation he has given of the limiting partition function for a simple cubic array of hard attractionless spheres compressed toward the limit of complete mutual contact, and with the conclusion which it establishes, that $3R$ is the correct theoretical fluctuation entropy for this case, appropriate to the choice of $l^3(1-\theta^{\frac{1}{3}})^3/N$ as the elementary cell. Rice's derivation also makes it possible to see where my "superficially straightforward" generalization of the one-dimensional case to three dimensions fails in this application. The latter corresponds, for the present model and for distinguishable particles, to letting each atom permute only with other atoms in the same linear arrays with it in the x, y, and z directions. A correct method of counting, permitting all $N!$ permutations, reproduces both Rice's mathematics and his result.

When the system becomes more expanded, the motions become too complicated for simple analytical discussion. There are doubtless several ways of "breaking down" the process by which the fluctuation entropy decreases as θ decreases, and the picture given here by Rice is very instructive in throwing light on one of them.

Rice and I have never disagreed on the physical occurrence of a considerable amount of fluctuation entropy in a real solid for which any intuitively "natural" choice of cell size is made. I agree with him completely as to the "naturalness" of choosing a definition of cell size which will be most appropriate to the purpose one has in view. I now agree with him also in accepting as significant the closeness of the agreement between the fluctuation entropy found, for his cell size, in solid argon and the theoretical value $3R$ which he has established.

The Tetrahedral P_4 Molecule

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April 15, 1946

THE methods developed by Pauling[1] in his treatment of the tetrahedral bond orbitals of carbon (and applied by him and others to a number of individual cases) have been extended and systematized by Kimball[2] into the theory of directed valence. This scheme serves to predict the bond configurations for covalent molecules with remarkable success.

One of the few remaining anomalies is the tetrahedral P_4 molecule (with its analog As_4). The bond angles for a trivalent P atom might be expected to be somewhat over 90°, as typical p bonds, and, in fact, all other compounds which have been investigated show angles in the neighborhood of 100°[3]. Pauling[3] has suggested that the P_4 molecule is merely a strained structure, but the great amount of distortion involved seems to render this explanation improbable. The purpose of this note is to point out a set of orbitals with more suitable bond angles.

The symmetry group of the three bonds extending from one P atom is C_{3v}, and from group theoretical considerations we can reduce the possible orbitals to p^3, sp^2, pd^2, sd^2. The bond angles for p^3 are obviously 90°, while for sp^2 and sd^2 they are 120°. The combination $p_s d_{xz} d_{yz}$, as for example in the set:

$$\psi_1 = 1/\sqrt{3}\psi p_z + \sqrt{2}/\sqrt{3}\psi d_{xz}$$
$$\psi_2 = 1/\sqrt{3}\psi p_z - 1/(6)^{\frac{1}{2}}\psi d_{xz} + 1/\sqrt{2}\psi d_{yz}$$
$$\psi_3 = 1/\sqrt{3}\psi p_z - 1/(6)^{\frac{1}{2}}\psi d_{xz} - 1/\sqrt{2}\psi d_{yz}$$

yields bond angles of 66°26′. This is the smallest possible angle for orbitals involving s, p, and d states only. The bond-forming strength (in Pauling's terminology) is 2.29, compared to 1.73 for pure p orbitals.

Some distortion is still required to compress these angles to 60°, but the strain is not now excessive. The advantage gained in replacing a triple bond by three single bonds may be used to account for the promotional energy required to produce a pd^2 structure from the p^3 ground state, and the stability of P_4 relative to P_2.

The above explanation sheds no light on the 60° bond angles found in carbon compounds, but it does account for the absence of a tetrahedral nitrogen molecule.

[1] L. Pauling, Proc. Nat. Acad. Sci. **14**, 359 (1928).
[2] G. Kimball, J. Chem. Phys. **8**, 188 (1940).
[3] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1944), second edition, p. 80.

Ultra-High Frequency Denaturation of Proteins

GEORGE A. BOYD
University of Rochester, Rochester, New York
April 18, 1946

ELECTROMAGNETIC waves in the ultra-high frequency range offers a new method for the study of protein-type molecules in the following suggested manner. From dielectic studies it is known that protein molecules are not rotated by frequencies above 10^7 cycles per second (below 30 meters). However, atomic and electronic polarization of the proteins do occur at the higher frequencies.

During each half-cycle, polarization on the molecule builds up to a peak and decays to zero. This produces a pulsating strain of twice the frequency of the electromagnetic wave. The pulsating strain will place the molecule in forced vibrations except at a resonant frequency, f_r, where the molecular energy absorption will rise sharply. The frequency f_r will depend upon whether the entire molecule vibrates as a two-body oscillator with each half of the mass of the molecule acting as one body or whether a prosthetic group and the remaining portion act as the two bodies. Because of the low strength of the hydrogen cross bonds and the small number required to be broken for denaturation, it is probably that at polarization resonance sufficient energy will be absorbed to denature the protein for the first type of vibration. Denaturation will result for the second type of vibration if the prosthetic group is broken off.

Now let us assume that each protein molecule of our laboratory experience is characterized by a unique energy state. For example, let us suppose that egg albumin has the energy E_1, and lactoglobulin, the energy E_2 and that each energy state will resonate with one particular frequency. Thus, there will be a frequency f_{r1} which will denature egg albumin and another frequency f_{r2} which will denature lactoglobulin. It then follows that each of the proteins, enzymes, viruses, genes, and other protein-like molecules can be denatured by frequencies which are related to their energy states. This would lead to a systematic identification of the molecules by their resonant frequencies.

In this connection it seems that we should not conceive of a large number of lactoglobulin molecules, for example, as having identical energy states. It is perhaps more probably that these molecules have a distribution of energy states, say a normal distribution with the mean state having the energy E_2. Thus, the question arises as to the sharpness of the effect of the resonant frequency, i.e., how broad is the band of energy states about the mean which will be denatured by f_{r2}.

We do not know how to determine this band width at present but the concept is of value in setting up biological experiments. Let us assume two proteins, for example, egg albumin and lactoglobulin with mean energy states E_1 and E_2, respectively, with distributions of states such that the denaturable band of states do not overlap. If we irradiate the two proteins in a common solution with a frequency f_{r1}, which will resonate with the band of states about E_1, but does not resonate with the band about E_2, we can visualize the denaturation of egg albumin without the denaturation of the lactoglobulin. There follows the

implications that a virus could be denatured without denaturing the proteins of the host, or that the energy state of one protein, enzyme, or gene could be changed without changing the states of neighboring molecules having different energies.

The Recognition of Phase Transitions in Adsorbed Films on Solids

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IN a recent note Jura, Loeser, Basford, and Harkins[1] have given evidence of a first-order phase transition taking place in a film adsorbed at a solid/vapor interface (*n*-heptane on silver). This is not, however, the first case of its kind to come to light, earlier instances having been reported from the University of Egypt where a study was made of the *swelling* effects which accompany adsorption on charcoal; water (23.5°C)[2] and methanol (0°C)[3] are cases in point.

The purpose of this note is to draw attention to the advantages which accrue in studies of the molecular structure of films on solids when the adsorbent is used in the form of a block which responds elastically by dimensional changes to the pressure F in the adsorbed films. The form of relation between F and the quantity adsorbed per g (s) can then be determined in two ways, *viz*: By direct measurements of the dimensional changes which accompany adsorption (Method I); and by use of Gibb's equation in its integrated form $F=(RT/M\Sigma)\int_0^p s\,d\log_e p$ (Method II); here p is the pressure of vapor, M its molecular weight, Σ the area per g of adsorbent. In Method I it is necessary first to establish that the adsorbent block does in fact respond elastically to changes of F. This done, however, the method gives far more reliable information than Method II as to phase relationships.

The statement of Brunauer[4] that in the experiments referred to my colleagues and I "unfortunately did not measure the adsorption isotherms of the vapours they used in the expansion experiments" is contrary to fact. We did, however, consider that Method I gave more reliable results than II because: (1) Unless a region of obedience to Henry's law can be established experimentally, the integration of the isotherms in the region of low pressures is not merely difficult but hazardous, especially if transitions occur. (2) We were unable to satisfy ourselves that Gibb's equation was obeyed over regions of phase transition, even when "time" effects and hysteresis were absent.[2, 3]

By Method I it was established that: (1) films adsorbed from vapors on the charcoal blocks used were mobile, and obeyed similar equations of state to films at liquid/gas interfaces;[5] (2) definite phase transitions occurred;[2, 3] (3) metastable films were of frequent occurrence, transition to a stable state manifesting itself by a *contraction* signifying increase of interfacial energy at constant adsorption;[2, 3] (4) while some adsorbed phases could be classed as "gaseous"* and some "liquid," in other cases the behavior was intermediate;[2, 3, *] (5) that a two-dimensional condensed phase does not necessarily confer complete wettability nor render capillary condensation in cavities inevitable;[6] (6) that film thickening occurs with some adsorbates at quite small relative pressures.[3, 7]

These conclusions—perplexing though they appeared when first published—have been generally confirmed by later work, notably by Jura, Harkins, and collaborators in the course of their elaborate investigation. The general similarity of phase relationships at solid/gas and liquid/gas interfaces has been stressed by Gregg,[8] who also emphasizes some of the difficulties attaching to Method II.

* In the papers quoted these were referred to as "equilibrium" or "annealed" films to avoid implications as to their classification. Their properties were, however, fully described (see D. H. Bangham, Proc. Roy. Soc. A **147**, 175 (1934)).

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[6] Bangham and Razouk, Trans. Faraday Soc. **33**, 1463 (1937).
[7] Bangham, Proc. Roy. Soc. A **147**, 175 (1934).
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Aggregational States in Adsorbed Films on Incompletely Wettable Solid Surfaces

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IF a solid surface fails to provide nuclei of condensation for a saturated vapor (i.e., supersaturation can occur), the adsorbed film must necessarily be in a state of aggregation different from the bulk liquid. If the bulk liquid is brought into contact with the solid there will be a finite contact angle.

It is not generally recognized that such saturated films adsorbed at incompletely wettable surfaces are usually of more than unimolecular thickness. Charcoal and methanol[1, 2] charcoal and water,[1, 3] graphite and water,[4] mica and benzene[5] are cases in point. De Boer has recorded other instances of essentially the same phenomena but in which the bulk adsorbate was solid (iodine on calcium fluoride;[6] caesium on calcium fluoride[7]). Earlier instances in which the adsorbent was liquid (water on mercury[8]) have been reported by Frumkin and co-workers.

It is remarkable that, where full data are available, the films at saturation frequently appear to be limited to about three molecules in thickness.[2, 3] Even where the isotherms are sigmoid and rise steeply near saturation (this being the common type for non-porous solids) they converge to an asymptote *beyond* saturation pressure and the saturation adsorption appears limited to about four molecular layers. The data of Palmer[9] for various organic vapors adsorbed on vitreous silica (the surface area of which was measured independently) provide numerous examples.

For explanation of such steeply rising isotherms (convex to pressure axis) we must clearly think in terms of a *patterned assembly* of adsorbed molecules, the interaction be-

tween which and the solid exceeds the sum of its interactions with an equal number of isolated molecules. The contact angle measures the incongruence of this pattern with that in the normal liquid and at the liquid/vapor interface. Substances completely wettable by water, therefore, are those upon which the pattern of adsorbed water molecules resembles that of the molecules of ordinary water or can fade imperceptibly into it. Incompletely wettable surfaces are not necessarily those which do not adsorb water, but *those on which the pattern is incompatible with that of normal water*. It is highly improbable that this pattern can be identified with that of ordinary ice, since this already exists in water at room temperature, and there is no evidence that contact angles decrease markedly below 4°C. Hysteresis of the contact angle (where real, and not due to contamination) would imply that the adsorbed film can exist in either of two configurations of equal stability.

By the use of a simple technique[10] it has been found possible to build up adsorbed layers of water and of organic vapors on mica to *visible* thickness (from supersaturated vapors) and demonstrate their incongruity with the normal liquids. The differences in behavior between water and such substances as benzene and carbon tetrachloride were too slight to suggest that the more general aspects of the phenomena depend on the hydrogen-bond structure peculiar to water.

Though the heat of adsorption in the outer layers is not necessarily equal to the normal latent heat (with methyl alcohol on charcoal it exceeds it) there are other cases where the difference is small, indicating that the "abnormality" lies in the entropy rather than in the energy of the film.

These observations may be helpful in connection with the theory of *solutions* since they offer suggestions as to the nature of the configurational changes which take place in the near neighborhood of solute molecules.

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Sedimentation Equilibria of Polydisperse Non-Ideal Solutes

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THE interpretation of equilibrium ultracentrifuge data for solutions of extended long chain molecules has been rendered difficult in the past by pronounced deviations from Henry's law at very low concentrations. This difficulty can be overcome by taking account of the deviations from ideality, using thermodynamic data from osmotic pressure measurements.

Consider a column of solution of unit cross section and length dx, in a centrifugal field. At equilibrium, the change in potential energy in moving c_x grams of material through the distance dx to a point where the concentration is c_x+dc_x will be balanced by the work done against the osmotic pressure difference $(\partial p/\partial x)dx$.

Let

$$p=(RT/M_{nx})c_x+b'c_x^2 \tag{1}$$

where p = osmotic pressure, in consistent units and M_{nx} is the number average molecular weight of material at distance x.

Then

$$c_x(1-\bar{V}\rho)\omega^2 x dx=(\partial p/\partial x)dx. \tag{2}$$

Now differentiating (1) and remembering that

$$M_{nx}=\frac{\Sigma_i c_i}{\Sigma_i c_i/M_i},$$

we obtain

$$\Sigma_i c_i\omega^2 x(1-\bar{V}\rho)=RT\Sigma_i\frac{dc_i}{dx}\frac{1}{M_i}+2b'\frac{dc_x}{dx}\Sigma_i c_i. \tag{3}$$

This can be considered to be the sum of i equations, so that

$$c_i\omega^2 x(1-\bar{V}\rho)=\frac{RT}{M_i}\frac{dc_i}{M_i}+b_i'\frac{dc_x}{dx}c_i, \tag{4}$$

where

$$2b'\Sigma_i c_i=\Sigma_i b_i' c_i.$$

It is to be noted that the sedimentation of each species is affected by the presence of the others. It is assumed that $b_i'=2b'$, as supported by the theory of Scott and Magat[1] and in the absence of evidence to the contrary. Proceeding from this point in a manner similar to that of Lansing and Kraemer[2] expressions for M_{wx} and M_{zx} are obtained, as follows:

$$M_{wx}=\frac{\alpha' Z}{c_x(2Ax-B\alpha' Z)}=\frac{\frac{\alpha' B}{2A}\frac{Z}{x}}{Bc_x\left(1-\frac{\alpha' B}{2A}\frac{Z}{x}\right)} \tag{5}$$

and

$$M_{zx}=\frac{\ln\frac{Z_2x_1}{Z_1x_2}-\ln\left(\frac{1-\alpha' BZ_2/2Ax_2}{1-\alpha' BZ_1/2Ax_1}\right)}{A(x_2^2-x_1^2)-B(c_2-c_1)}. \tag{6}$$

In these expressions,

$$A=\frac{(1-\bar{V}\rho)\omega^2}{2RT}$$

$$\alpha'=\frac{1}{Gab\alpha}=\frac{dc/dx}{Z}$$

$$B=\frac{20gb'}{RT},$$

when c_x is measured in g/100 g solution and

$$b' \text{ in } \frac{\text{mm solvent}}{\left(\frac{\text{g}}{100\text{ g}}\right)^2}.$$

TABLE I.

Experiment	Uncorrected M_z	Concentration g/100 g	R.P.M.	Concentration ratio between ends of cell	Corrected M_w	Corrected M_z
23	95,000	0.108	4700	4	97,000	153,000
24	86,000	0.108	6270	10	107,000	141,000
25	120,000	0.072	6440	10	108,000	150,000

Osmotic pressure	Sedimentation data, corrected			Theoretical
M_n	M_w	M_z	M_z/M_w	M_z/M_w
50,000	104,000	148,000	1.42	1.50

The averaging formula for M_z becomes

$$M_z=\frac{\int_a^b \frac{M_{zz}Zdx}{1-\alpha' BZ/2Ax}}{\int_a^b \frac{Zdx}{1-\alpha' BZ/2Ax}}.$$

The averaging formula for M_w remains unchanged. Some results obtained with the equilibrium ultracentrifuge for the system polystyrene-carbon tetrachloride are given below in Table I.

The constant B in c.g.s. units for carbon tetrachloride-polystyrene (c_z in g/100 g) was 0.1705×10^{-4}. The molecular weight distribution as calculated from the assumed reaction mechanism gives

$$M_n: M_w: M_z = 1:2:3.$$

Also it has been found mathematically possible to calculate the differential weight distribution curve of the polymer from one experiment in the equilibrium ultracentrifuge, provided $b_i'=2b'$. The method is similar to that of Rinde.[3]

However, the calculations are extremely tedious and they are of doubtful accuracy when based on only one experiment. In addition to this the curve will be skewed to a certain extent depending on the difference of b_i' from $2b'$.

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